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Zoology. — *"On the fresh-water fish-fauna of New Guinea"*. By Prof. MAX WEBER.

(Communicated in the meeting of November 24, 1906).

In the year 1877 there appeared a "Quatrième mémoire sur la faune ichthyologique de la Nouvelle-Guinée", written by P. J. BLEEKER and containing 341 species. These species are exclusively marine and brackish-water fishes and shew clearly, as might be expected, that the littoral fish-fauna of New Guinea belongs to the great Indo-Pacific fauna which extends from the East coast of Africa to the islands of the Western Pacific.

The same result is arrived at from the lists published by W. MACLEAY in 1876 and 1882, which treat of the fishes of the South coast of New Guinea and Torres Straits. But none of these lists accomplished what BLEEKER desired, namely, to give some insight into the nature of the fresh-water fish-fauna of New Guinea. The information which BLEEKER desired was partly supplied by certain communications, published by W. MACLEAY, E. P. RAMSAY, J. DOUGLAS OGILBY, A. PERUGIA and G. BOULENGER, about fishes caught in the Strickland, Goldie and Paumomu rivers, and in a number of rivulets all situated in the south-eastern part of the island. The number of fishes mentioned amount to about 30, but so long as the fish-fauna of German and Dutch New Guinea remained unknown, it was impossible to give a complete idea of the ichthyological fauna of this big island.

This was the more to be regretted inasmuch as fresh-water fishes are of very great assistance in solving zoo-geographical problems. In using them for this purpose we should however keep well in mind the following points.

If in regions, at present separated by the sea, identical or closely allied fresh-water forms are found, to which the sea affords an insurmountable barrier, one may freely draw the conclusion that these regions were formerly either directly or indirectly connected. Among the fresh-water fishes there are however whole categories which cannot be used as factors in such an argument or only with great caution. These are the migratory fishes and those that can live also in brackish water and indeed even in sea-water.

The so-called law of E. VON MARTENS states that from the Poles to the Equator the number of brackish water animals increases. This is also true for fishes and especially for those of the Indo-Australian Archipelago, and in a very remarkable degree for those of the islands east of Borneo and Java. The great Sunda Islands

in consequence of their former connection with the continent of Asia possess a fish-fauna of which the most important elements, both as regards quality and quantity, had no chance of further distribution in an eastern direction. The rivers of the eastern islands of the Archipelago were therefore almost devoid of fishes, and offered a good place of abode for such forms as, though denizens of the sea or of brackish water, possessed sufficient capacity for accommodating themselves to a life in fresh-water. The competition of those Asiatic forms (Cyprinidae, Mastacembelidae, Ophiocephalidae, Labyrinthici etc.), originally better fitted for a fresh-water life, failing, everything was in favour of the immigrants from the sea. The river-fishes of Celebes favour this view, as also does all that we know about the fishes of Ternate, Ambon, Halmahera, etc.

We observe the same phenomenon in the fresh waters of Australia. These however contain also indigenous forms, partly very old, partly younger forms; the latter were obviously, at least in part, marine immigrants, which have accommodated themselves so entirely to a fresh-water life as to adopt the characters of fresh-water fishes.

The fauna of Australia enjoy at present a general and vivid interest — are there not even people who believe that the cradle of mankind stood there? A remarkable point of interest in the study of its fauna is the question how long Australia has been isolated from other parts of the globe. New Guinea plays a prominent rôle in answering this question.

It is therefore a welcome fact that the Dutch New Guinea Expedition of 1903 under the direction of Prof. A. WICHMANN has brought home, besides other treasures, a large collection of fishes from different lakes and many rivers and rivulets, giving us a good insight into the fresh-water fauna of the northern part of the island. It was of great help to me, while studying this collection, that I was able to make use of the fishes collected in the brackish water at the mouth of the Merauke river, by Dr. KOCH the medical man of the Royal Geographical Society's Expedition to South New Guinea. The results of this investigation will be published elsewhere, but some more general conclusions may be mentioned here.

When we reckon up all the fishes known up to the present date from the lakes, rivers, and rivulets of New Guinea, we find that their number amounts to more than 100 species, but only about 40 of these were found exclusively in fresh-water.

A careful examination shews further that the latter species, with a few exceptions, are either known from brackish or sea water at other places, or that their nearest relatives may be found in brac-

kish or sea water. New Guinea shews clearly the fact that immigration from the sea or from brackish water has played and perhaps still plays a predominant part in the populating of its rivers.

Let us now return to the point at issue: namely, that the marine fish-fauna of New Guinea forms part of the great Indo-Pacific fish-fauna and particularly of that of the Indo-Australian Archipelago. Keeping this in mind one might be inclined to draw the conclusion that there is not much to be learned from the fauna of the rivers of New Guinea concerning the history of this island. Such a conclusion however would be erroneous, for it is clear that the very fishes which are characteristic of the fresh-water of New Guinea belong:

1. to genera which outside New Guinea are known only from Australia (Pseudomugil, Rhombatractus, Melanotaenia, Eumeda);

2. or to genera nearly related to exclusively Australian genera. Lambertia for instance is nearly related to Eumeda; Glossolepis to Rhombatractus and the three new species of Apogon are closely allied to Australian ones. Finally the species of Hemipimelodus from New Guinea form a special group, distinct from those of the neighbouring Indian Archipelago. Everything that gives to the fresh-water fish-fauna of New Guinea a character different from that of the Indian Archipelago is at the same time characteristic of Australia. Twelve of its species belonging to the genera Pseudomugil, Rhombatractus, Melanotaenia, Glossolepis, belong to the family or subfamily of the Melanotaenidae, only known from Australia. I do not hesitate therefore to maintain that the river-fishes of New Guinea belong to two groups:

1. A fluvio-marine group, which is Indo-Australian or, if one prefers, Indo-Pacific and which may also be met with, for instance, in Ambon or Celebes. To this category belongs also Rhiacichthys (Platyptera) novaeguineae Blgr. discovered by Pratt in mountain rivers of the Owen Stanley Range four thousand feet high. Boulenger speaks of the discovery of a fish of the genus Rhiacichthys "so admirably adapted to life in mountain torrents" as highly interesting. He tells us that the closely allied Rhiacichthys asper C. V. is known from Bantam, Celebes and Luzon. This is likely to create the impression that Rhiacichthys novaeguineae does not belong to this category, but is a species whose nearest relative is confined to rivers in regions occupied by the Asiatic fauna. Rhiacichthys asper however, differing but little from Rhiacichthys novaeguineae, was also found by Bleeker in Sumatra and, what is far more interesting, it occurs, according to Günther, also in Wanderer Bay on the island of Guadalcanar in the Solomon Islands — in "fresh-water". At all events it is thus found close to the sea. This

is also true for a specimen which I described from Ambon and still more so for a specimen that I caught near Balangnipa in the lower part of the Tangka, close to its mouth in the gulf of Boni. The water was here already brackish and ran slowly. Rhiacichtys has therefore a very wide distribution, it does not fear brackish water, and its presence in New Guinea loses therewith much of its importance.

2. The second group, the characteristic element, is Australian. This last group requires further explanation as to its origin. In the present state of things, now that New Guinea is separated from Australia by Torres Straits, these offer a barrier impassable to those fishes which I called characteristic. Some species of Rhombatractus and Melanotaenia may it is true, descend to the mouth of the river and be able to endure even slightly brackish water, but none of the 24 recorded species is known from the sea. The barrier can therefore not be bridged by the group of islands in the Torres Straits. They are too poorly supplied with fresh-water and far too strictly coral islands, even when we leave out of consideration the fact that they are separated from each other, from New Guinea and from Australia by broad tracts of sea with a high salt percentage and strong tidal currents. The simultaneous presence of these characteristic forms in New Guinea and in Australia cannot be explained otherwise than by the existence of a more solid and extensive connection in former ages. This connection must have been so far back in the past that, to take an instance, the representatives of the abovenamed Melanotaeniideae had time to separate themselves specifically. And this actually happened; for among the 12 species of Melanotaeniidae already known from New Guinea and among the 12 species described from tropical or sub-tropical Australia not one is common to the two regions, although the differences between some species are very small. On the other hand therefore it cannot have been so very long ago from a geological point of view that this connection between Australia and New Guinea existed. How long a time may have elapsed since that period is at present a matter of hypothesis. But if zoo-geographical and more particularly ichthyological experience may venture an opinion, I should seek the period of this connection not earlier than in the pliocene, and the breaking up of it in the pleistocene. Other zoological observations may perhaps be in favour of this supposition.

It will be a long time yet before the last word is spoken on this question. We may express the hope that the new expedition to Dutch Southern New Guinea under the guidance of Dr. H. A. Lorentz, which intends to investigate especially its big rivers, will bring us further light.

Chemistry. — *"On Lupeol"* [1]). By Dr. N. H. COHEN. (Communicated by Prof. P. v. ROMBURGH).

(Communicated in the meeting of November 24, 1906).

Notwithstanding the many and beautiful researches of several chemists, the structure of cholesterol, which is important also from a physiological point of view, is far from being known. Therefore, Prof. VAN ROMBURGH invited me to investigate a substance closely connected with the same, namely lupeol, a phytosterol. For the phytosterols may be included with the cholesterols in one common group "the cholesterollic substances". The original intention was to study the alstol found by SACK [2]) in "bresk" [3]). From the "bresk" investigated by me, alstol, alstonol and *iso*alstonol could not be isolated, although SACK claims to have found them in the same, but I obtained α- and β-amyrin and lupeol. It appeared afterwards that SACK's alstol is not a chemical individual.

Lupeol was first found by LIKIERNIK [4]) in the skins of lupin seeds; afterwards SACK [5]) met with it in the bark of Roucheria Griffithiana, whilst VAN ROMBURGH and VAN DER LINDEN [6]) demonstrated its presence as a cinnamate in the resin of Palaquium calophyllum. Finally, VAN ROMBURGH proved that TSCHIRCH's [7]) crystal-albane simply consisted of lupeol cinnamate. The lupeol was prepared from "bresk" by extracting the same first with boiling alcohol. On cooling, a white mass was deposited which, without any further purification was saponified with alcoholic potassium hydroxide. The saponified product was then benzoylated with benzoyl chloride and pyridine and the reaction product treated repeatedly with acetone by heating just to boiling on the waterbath and then filtering off without delay.

Finally, a lupeol benzoate was left, which after repeated recrystallisation from acetone, consisted of fine, flat needles; m.p. 265°—266°, (corr. 273°—274°).

Found C	83.71—83.81	Calculated for $C_{38}H_{54}O_2$	84.07
H	10.41—10.36		10.03

These, like all subsequent combustions, were made with lead chromate.

$$[\alpha]_D = +60°,75 \text{ in chloroform.}$$

[1]) For a more elaborate description see Dissertation N. H. COHEN. 1906, Utrecht.

[2]) SACK. Diss. 1901, Göttingen.

[3]) Bresk or djetulung is the dried milky juice of some varieties of Dyera.

[4]) Ztschr. f. physiol. Chem. **15**. 415 (1891).

[5]) SACK l. c.

[6]) Ber. **37**. 3440 (1904).

[7]) Arch. der Pharm. **241**. 653 (1903).

By saponification of lupeol benzoate with alcoholic potassium hydroxide and recrystallisation from alcohol or acetone, the lupeol was obtained in the form of fine, long needles m.p. 211°, (corr. 215°).

Found:	C	84.62	84.65	84.40	84.50	Calculated for $C_{31} H_{50} O$ 84.85
	H	11.78	11.93	11.82	12.02	11.49

$[\alpha]_D = + 27°,2$ in chloroform.

In the first place it seemed to me of importance to ascertain whether double bonds occur in lupeol. Therefore, a solution of lupeol in carbon disulphide was treated with a solution of bromine in the same solvent. Hydrogen bromide was evolved. By recrystallising the reaction product from methyl alcohol, needles containing 1 mol. of the latter are formed. The melting point of this substance, dried at 100°, was 184°, (corr. 185°).

Found:	I	II	III	IV	V	VI	VII	calc. for $C_{31} H_{49} OBr$.
C	72.14	72.30						71.90
H	10.26	10.07	CARIUS			LIEBIG		9.55
Br			14.48	14.50	15.40	15.07	14.67	15.45

$[\alpha]_D = + 3°,8$ in chloroform.

Most probably, a monosubstitution product had formed and I now tried to obtain an additive product of the benzoate. When dissolved in a mixture of glacial acetic acid and carbon disulphide and then treated with a solution of bromine in glacial acetic acid, it yielded, after spontaneous evaporation of the carbon disulphide, beautiful leaflets. On extracting this product with boiling acetone a less easily soluble substance was left, which proved to be a *monobromide*. After repeated recrystallisation from aethyl acetate, I obtained fine, thick crystals which when melting were decomposed. Placed in the bath at 240° it melted at 243°.

Found	I	II	III	IV	V	VI	VII	VIII	IX	X
C	72.62	72.90	72.58	72.46	72.59					
H	8.85	8.88	8.72	9.09	8.84	CARIUS			LIEBIG	
Br						13.14	13.04	12.97	13.40	13.01

Calculated $C_{38} H_{53} O_2 Br$, C = 73.38, H = 8.61, Br = 12.87.

$[\alpha]_D = + 44°,9$ in chloroform.

The bromine atom is contained in the lupeol nucleus, because on saponification an alcohol containing bromine, and benzoicacid are formed.

The more readily soluble portion crystallises from acetone in beautiful leaflets. It is also a monobromide but could not with certainty be characterised as a chemical individual.

One of the means to trace the structure of a substance is the gradual destruction by oxidation.

The lupeol was, therefore, oxidised with the KILIANI mixture[1]). Lupeol dissolved in benzene was shaken with a weighed quantity of the oxidising liquid, 6 atoms of oxygen calculated for 1 mol. of lupeol. Titrations of the oxidising liquid with potassium iodide and sodium thiosulphate showed, that after six hours one atom of oxygen had been consumed and as the amount of chromic acid did not diminish any further, this one atom had been taken up quantitatively. The oxidation product, which crystallised from alcohol in beautiful, thick needles, melted at 169° (corr. 170°) and proved to be a *ketone*, to which I gave the name of *lupeon*.

Found	C	84.95	84.91	85.07	84.76	Calc. for $C_{31}H_{48}O$	85.24
	H	11.64	11.81	11.62	11.61	11.59	11.09

$[\alpha]_D = +63°,1$ in chloroform.

Dr. JAEGER was kind enough to examine the crystalform of the lupeon. It belongs to the rhombo-bipyramidal class. A complete description will appear elsewhere.

With hydroxylamine an oxime of the lupeon was obtained, which is but little soluble in alcohol.

Recrystallised from ethyl acetate, it forms white, soft, light needles, which are decomposed when melting. Placed in the bath at 278°, they melt at 278°,5.

Found	C	81.98	Calc. for $C_{31}H_{48}NOH$	82.41
	H	11.44 (with lead chromate)		10.94
	N	3.08		3.11

$[\alpha]_D = +20°,5$ in chloroform.

Bromine dissolved in glacial acetic acid added to a solution of lupeon in the same solvent gave hydrogen bromide and a dibromide, which was deposited from the acid. Recrystallised from a mixture of benzene and glacial acetic acid it consisted of beautiful, hard needles, which were decomposed when melting. Placed in the bath at 253° the melting point was 254°.

Found	I	II	III	IV	V	VI	VII	VIII	IX	X
C	62.31	62.71	62.50	62.30						
H	8.13	8.26	8.05	8.06	CARIUS				LIEBIG	
Br					26.88	26.91	27.08	26.85	27.35	27.23

Calc. for $C_{31}H_{46}OBr_2$, C = 62.58, H = 7.80, Br = 26.90.

$[\alpha]_D = +21°,4$ in chloroform.

When dissolved in ether, lupeon gave with hydrogen cyanide under the influence of a trace of ammonia a cyanohydrin, which

[1]) Ber. **34**. 3564 (1901).

after some time deposited in the form of beautiful, thick needles. This substance is decomposed at a higher temperature and also on melting. Placed in the bath at 192°, it melts at 194°. By collecting the hydrogen cyanide liberated on heating in aqueous potassium hydroxide and then titrating with silver nitrate I determined the nitrogen content.

Found:	I	II	III	IV	V	VI	VII	calc. for $C_{33}H_{49}ON$
C	82.63	82.76						82.86
H	11.25	11.26	copper oxide		lead chromate	titrated		10.66
N			3.92	3.94	3.30	2.87	2.70	3.03

One mol. of cyanohydrin gave, with one mol. of ethyl alcohol and one mol. of hydrogen chloride, a substance, which, when placed in the bath at 230°, melted at 235°; as shown by a combustion, this was not, however, the expected ethyl ester of the corresponding acid. This substance has not been investigated further.

Lupeol benzoate treated in the same manner as lupeol with the KILIANI mixture was not affected. Lupeon dissolved in benzene and stirred with the mixture for four hours at 40° also remained unaltered.

By the action of chromic anhydride on lupeon at a higher temperature, acid products were formed, which could not be obtained in a crystalline state.

The neutral oxidation product of lupeol with potassium permanganate and sulphuric acid consisted of a mixture, which could be separated only with extreme difficulty. Excepting lupeon no well-defined substance could be isolated from it. As SENKOWSKI [1]) had obtained phthalic acid from cholic acid by oxidation with alkaline permanganate, I treated 23 grams of lupeol in the same manner, but it suffered complete destruction. This fact does, therefore, *not* favour the idea of a *benzene nucleus* in lupeol.

By the oxidation of an acetic acid solution of lupeol acetate with chromic acid, I obtained a product which, on analysis, gave figures which agree satisfactorily with the calculated values for $C_{33}H_{52}O_4$.

Placed in the bath at 285° it melted at 295° to a dark brown mass.

In alcoholic solution this substance did not turn blue litmus red, not even on diluting with water, but still it could be titrated very readily with alcoholic potassium hydroxide, phenolphtalein being used as an indicator. Assuming that one mol. consumes one mol. of KOH the titrations pointed to a molecular weight of 521 and 524, the formula $C_{33}H_{52}O_4$ representing 512,5.

Found:					calculat. for $C_{33}H_{52}O_4$	
	C	77.59	77.23	76.87 77.24		77.28
	H	10.75	10.49	10.09 10.79		10.23

[1]) Monatsh. f. Chem. **17**. 1 (1896).

On saponification with alcoholic potassium hydroxide a substance was obtained which crystallised from ether in needles. Placed in the bath at 260°, the melting point was 263—265°. In regard to litmus this substance behaves like the unsaponified product, but it may be again titrated with alcoholic potassium hydroxide and phenolphthalein. From these titrations the molecular weight was found to be 452 and 461; the formula $C_{31}H_{50}O_3$ represents 470,5.

Found: C 78.42 78.61 calculated for $C_{31}H_{50}O_3$ 79.08
H 11.07 11.05 10.71

The potassium compound of this substance is soluble, with difficulty, in alcohol, and crystallises from this in needles.

On treating either the saponified or the unsaponified oxidation product the same compound was obtained, which seems to be a diacetylated substance. The results of the combustions, however, were not very concordant, but I have not been able to account for this.

Found: C 75.39 74.71 75.67 74.96 74.47 calcul. for $C_{35}H_{54}O_5$ 75.75
H 10.12 10.16 10.51 10.24 9.81

By boiling with excess of alcoholic potassium hydroxide and titrating with alcoholic sulphuric acid the molecular weight was found to be 549, assuming that the molecule contains two acetyl groups. The formula $C_{35}H_{54}O_5$ represents 554.5.

It is desirable to investigate more closely these oxidation products, which are so important in the study of lupeol, before trying to explain their formation.

Lupeol is not reduced by metallic sodium and boiling amyl alcohol; whereas lupeon is reduced by sodium and ethyl alcohol to lupeol. Therefore, if lupeon should possess a double bond, this is sure not to be in $\alpha\beta$-position in regard to the carbonyl group.

Neither lupeol, nor lupeol acetate dissolved in boiling acetone are acted upon by potassium permanganate. This behaviour does not agree with the theory of a double bond, but the presence of the latter in lupeol and lupeon could be satisfactorily demonstrated by means of HÜBL's iodine reagent. On the other hand the oxidation product $C_{32}H_{52}O_4$ no longer seemed to contain the double bond. On the strength of various combustions and bromine determinations, particularly of dibromolupeon, I consider $C_{31}H_{50}O$ to be the most likely formula for lupeol. The formula $C_{26}H_{42}O$ given by LIKIERNIK [1]) and SACK [2]) is certainly not correct.

Utrecht, Org. Chem. Lab. University.

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[1]) LIKIERNIK l. c.

[2]) SACK l. c.

Chemistry. — *"On α- and β-amyrin from bresk"* [1]). By Dr. N. H. COHEN. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of November 24, 1906).

Communications as to β-amyrin, which is present as acetate in "bresk" or "djelutung" have already been presented (These Proc. 1905, p. 544). Since then, I have prepared also β-amyrin cinnamate. This crystallises from acetone in small needles, which melt at 236°,5 (corr. 241°).

In addition to β-amyrin and lupeol another substance was obtained from "bresk", which proved to be identical with the α-amyrin found by VESTERBERG.

This substance crystallises from alcohol in long, slender needles; m.p. 185° (corr. 186°). VESTERBERG gives the melting point as 181—181°,5.

Found: C 84.22 84.30 calculated for $C_{30}H_{50}O$ 84.43
H 11.91 12.02 11.82

These, like all subsequent combustions have been made with lead chromate.

$[\alpha]_D = +82°,6$ in chloroform; in benzene was found $[\alpha]_D = +88°,2$.[2])

For the purpose of characterisation, different esters were prepared from α-amyrin.

α-Amyrin acetate was obtained by heating with acetic anhydride and sodium acetate. Recrystallised from alcohol it forms needle-shaped leaflets; m.p. 220—221°, (corr. 224—225°). VESTERBERG gives the melting point as 221°.

Found: C 81.85 82.27 81.79, calculated for $C_{32}H_{52}O_2$ 81.98
H 11.34 11.40 11.33 11.19

$[\alpha]_D = +75°,8$ in chloroform.

α-Amyrin benzoate was obtained with the aid of benzoyl chloride and pyridine. From acetone it crystallised in long, prismatic needles; m.p. 192°, (corr. 195°). According to VESTERBERG it melts at 192°.

α-Amyrin cinnamate, which has not yet been described was obtained like the benzoate. When recrystallised repeatedly from acetone it forms small hard needles which melt at 176,5—177°, (corr. 178°).

Utrecht. Org. Chem. Lab. Univ.

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1) For a more elaborate description see, Diss. N. H. COHEN. 1906, Utrecht.

2) VESTERBERG found in benzene $[\alpha]_D = +91°,6$.

Chemistry. — "*On substances, which possess more than one stable liquid state, and on the phenomena observed in anisotropous liquids.*" By Dr. F. M. JAEGER. (Communicated by Prof. FRANCHIMONT).

§ 1. The compounds now investigated belong to the series of fatty cholesterol-esters, which were the subject of a recent communication [1]). They are intended to supplement the number of the synthetic esters, studied previously and include: *Cholesterol-Heptylate*, *Nonylate*, *Laurate*, *Myristate*, *Palmitate* and *Stearate*. The *Palmitic* ester, as is well known, is also important from a physiological point of view, as it occurs constantly in blood-serum accompanied by the *Oleate* m.p. (43° C.) [2]).

I have prepared these compounds by melting together equal parts by weight of pure cholesterol and fatty acid, and purifying by fractional crystallisation from mixtures of ether and alcohol, or ethyl acetate and ether. The details will be published later on in a more elaborate paper in the "Recueil". The substances were regarded as pure, when their characteristic temperature-limits and the typical transformations occurring therein, remained the same in every particular, even after another recrystallisation, whilst also the solid phase, when examined microscopically, did not appear to contain any heterogenous components.

Most of these esters were obtained in the form of very flexible, tabular crystals of great lustre and resembling fish-scales; some of them, such as the *heptylate* and the *laurate*, crystallise in long, hard needles.

The investigation showed, that most of these esters of the higher fatty acids possess *three stable liquid phases*. Whereas, in the first terms of the series one at least of these anisotropous phases was *labile* in regard to the isotropous fusion, all three are now *stable* under the existing circumstances, although sometimes definite, irreversible transitions may still occur. It is a remarkable fact, that the stearate again exhibits an analogy with the lower terms, as it appears that only labile liquid-anisotropous phases may occur, or else none at all. A relation and similarity between the initial and final terms

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[1]) F. M. JAEGER, These Proc. 1906; Rec. d. Trav. d. Chim. d. Pays-Bas, T. XXIV, p. 334—351.

[2]) K. HÜRTHLE, Z. f. physiol. Chem. **21**. 331. (1895); The blood serums of: man, horse, ox, sheep, hog and dog were investigated.

of the homologous series is plainly visible here. In what follows there will be described, firstly, the thermic, and then the microscopic behaviour of these substances.

§ 2. **The Thermometric Behaviour of these Substances.**

Cholesterol-Laurate exhibits the following phenomena: The isotropous fusion L of this substance has still, at 100° the consistency of glycerol, and gradually thickens on cooling. At 87°.8 C. ($= t_3$) there suddenly occurs a peculiar violet and green opalescence of the phase, which commencing at the surface, soon embraces the whole phase. The still transparent thin-jelly-like mass quite resembles a coagulating colloidal solution; the opalescence is analogous to that often noticed in the separation of two liquid layers.

As the cooling proceeds, the opalescence colours disappear and the mass gradually becomes less transparent and also more liquid. It is then even thinner than the isotropous fusion L. This doubly-refracting liquid A now solidifies at 82°.2 C. ($= t_1$) to a crystalline mass S, accompanied by a distinct heat effect.

If, however we start with the solid phase S and subject the same to fusion, the behaviour is apparently quite different. The substance softens and yields after some time a thick doubly-refracting mass, which will prove to be identical with the phase A. On heating further the viscosity decreases, and at about 86° it becomes very slight. There is, however, no sign of opalescence this time. The turbid mass may be heated to over 90°, without becoming clear and now and then A seems as if solid particles are floating in the liquid phase. At 90°.6 C. ($= t_5$) everything passes into the isotropous fused mass L. The microscopical investigation shows, that between A and L another stable, less powerfully refracting liquid phase B is now traversed, and that, owing to retardation occurring, the phase S may be kept for a few moments adjacent to L, when A and B have already disappeared.

This is therefore, a case where a substance may be heated a few degrees above its actual melting point without melting.

It should, however, be observed that the order of the temperatures is here quite irreconcilable with the phenomena considered possible up to the present, with homogenous substances; the temperature of 90°.6, at which these crystals disappear in contact with L finds no place in the p-t-diagram of Fig. 1. Such a position of the said temperatures might be possible, when the system could be regarded as containing two components, for instance, if there was question of *tautomeric* forms which are transformed into each other with finite velocities. I think it highly probable that in all these substances,

"phenomena of retardation" play a great rôle; moreover the enormous undercooling which the phase *A* can undergo without transformation, proves this satisfactorily in the majority of these esters.

The different behaviour of the laurate on melting and on cooling the fused mass is so characteristic, that no doubt can be entertained as to the irreversibility of each series of transformations. Fuller details will be given below in the micro-physical investigation.

§ 3. *Cholesterol-Nonylate* forms at 90° an isotropous fused mass of the consistency of paraffin oil; on cooling to 89°5 a stable, greyish, doubly-refracting liquid *B* appears which, gradually thickening, passes into a second strongly doubly-refracting liquid phase *A*, — which transformation is accompanied with a brilliant display of colours. All three liquids are, however, quite stable within each specific temperature-traject. On melting, as well as on cooling the substance, they succeed each other in the proper order.

The viscous, strongly doubly-refracting, liquid phase *A* now becomes more viscous on cooling, and is finally transformed into a horny, transparent mass which exhibits no trace of crystallisation. Even after some hours, the often still very tenacious mass has not got crystallised. In the case of this substance it is therefore impossible to give the solidifying point or the exact temperature at which the heated mass begins to melt. The reason of this is, that the doubly refracting liquid *A* can be undercooled enormously and passes gradually into the solid condition without crystallising.

As the micro-physical research has shown, a spherolite-formation occurs afterwards suddenly in the mass, which ultimately leads to the complete crystallisation of the substance.

The velocity, with which such spherolites are formed appeared in some cases not to exceed 0.000035—0.000070 m.m. per second!

§ 4. *Cholesterol-Myristate*, at 80°, is still an isotropous, paraffin oil-like liquid. On cooling, it gradually becomes viscous; at about 82.°6 the glycerol-like phase then turns, with violet-blue opalescence, into a thick, strongly doubly-refracting mass *A* which, gradually assuming a thicker consistency, is finally converted into a horny mass, without any indication of a definite solidifying point. In this respect the substance is quite analogous to the previous one. On the other hand, on being melted, it behaves more like the laurate, in so far as it is converted into a double-refracting liquid *B*, before passing completely into *L*. The transition temperature cannot be determined sharply, but I estimate it at about 80°.

§ 5. *Cholesterol-Palmitate* at 80° is a clear, isotropous liquid as thick as simple syrup. On cooling, the isotropous phase is converted at 80° with green opalescence into a fairly clear, transparent, doubly-refracting jelly *A*, which rapidly assumes a thinner consistency, and becomes at the same time more turbid, and finally solidifies at 77.°2, with a perceptibte caloric effect, to a crystalline mass *S*. In this case also, a doubly-refracting phase *B* appears to be traversed when the mass is being melted, before the occurrence of the isotropous fusion *L*; I estimate the transition temperature at about 78°.

§ 6. With *Cholesterol-Stearate*, I did not succeed in demonstrating the occurrence of a doubly refracting liquid. The isotropous, thick-fluid fusion solidifies at 81° to well-formed crystals *S*.

§ 7. *Cholesterol-Heptylate* exhibits, in undercooled fusion only, one doubly-refracting liquid phase which is labile in regard to the solid phase *S*. The compound behaves, thermically, analogously to the caprylate. The temperature of solidification is at 110.°5, the transition-temperature of the labile doubly-refracting phase lies a little lower.

Of *Cholesterol-Arachate*, I could only obtain an impure product on which no further communications will be made. The ester could not be purified properly as it is not soluble to any extent in the ordinary solvents. The crude substance obtained does not seem to exhibit any anisotropous liquid phases.

§ 8. **Micro-physical behaviour of these substances.** If a little of the pure solid *cholesterol-laurate* is melted on an object glass to an isotropous, clear liquid *L*, and the same is allowed to cool very slowly, there is formed, usually, a very strongly doubly-refracting, liquid phase, gleaming with lucid interference colours. It consists of large, globular drops, which exhibit the black axial cross and, on alternate heating and cooling, readily amalgamate to a syrupy, highly coloured, but mainly yellowish-white liquid. This phase will be called *A* in future. On cooling, it gradually thickens, until no more movement of the mass is noticed, which continues to exhibit a granular structure. Around this mass an isotropous border liquid is found. At first I felt inclined to look upon this tenaceous, isotropous mass, which is visibly different from the fusion *L*, as a distinct phase differing from the fusion *A*. But on using a covering glass and pressing the same with a pair of pincers, or by stirring with a very thin platinum wire, I found that this border liquid is only

"pseudo-isotropous" (LEHMANN) and is, in reality, not different from *A*; only, the optical axes of the liquid crystals are all directed perpendicularly to the glass-surface. The other cholesterol-esters also exhibit this phenomenon. On further cooling, this phase *A* crystallises like the pseudo-isotropous border to a similar mostly spherolitic crystalline mass *S*.

Between the spherolites one often sees currents of the pseudo-isotropous border liquid.

If now the entire mass is allowed to solidify to *S*, and then again is melted carefully, it is at once transformed into the liquid *A*, recognisable by its high interference colours and its slow currents. Then, there appears suddenly a new, greyish liquid *B*, consisting of smaller individuals with a less powerful double refraction, which after a short time is replaced suddenly by the isotropous fusion *L*. If *L* is now cooled again, it is *A* which appears at once and *not* the phase *B*.

Only a very feeble, greyish flash of light, lasting only for a moment, points to a rapid passing of the phase *B*; it cannot, however, be completely realised now. On further cooling, *S* is formed suddenly, sometimes in plate-like crystals. When once crystallisation has set in, *S* will not melt when the mass is heated, as might have been expected, but actually increase in size of the crystals occurs, and the velocity of crystallisation is now many times increased. It must be remarked that the growing flat needles of *S* drive before them, at their borders, the liquid phase *A* amid violent currents. If the heating is now continued a little longer, we may notice sometimes, that whilst the little plates of *S* remain partly in existence, *A* passes first into the grey phase *B*, which then is converted into the isotropous mass *L*. We then have adjacent to *L* the solid phase *S*, *which therefore, may be heated above its melting point*, before disappearing finally into the isotropous fusion *L*.

All this shows, that the *laurate* possesses *three stable liquid phases* and also that the isotropous fusion being cooled, *B* is always passed over, but is realised when the solid phase is heated. All this is represented in the annexed *p-t*-diagram; the arrows, therefore, indicate the order of the phases traversed on melting and on cooling. The phase *A* in its quasi-immovable period may be kept a long time solid at the temperature of the room, and may be considerably undercooled before it passes into *S*. Notwithstanding its apparently solid appearance in that undercooled condition, *A* is still a tenaceous, thick liquid, as I could prove by stirring the mass with a thin platinum wire.

The point (t_3) agrees with the *opalescence* which occurs when

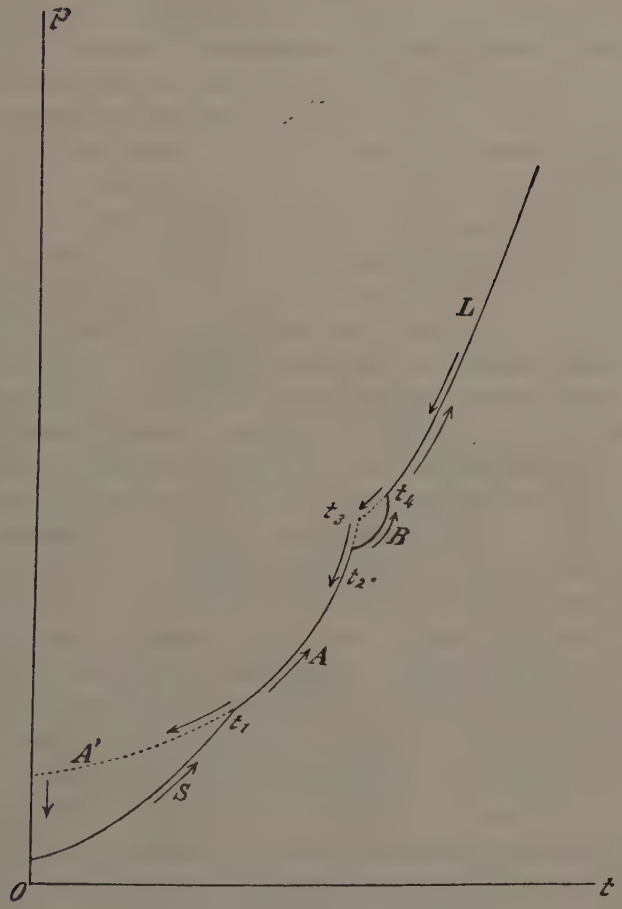


Fig. 1. Schematic *p-t*-diagram for Cholesterol-Laurate.

the isotropous fusion is cooled; this indicates, therefore, the moment *where the stable phase B is replaced by the as yet still less stable phase A*, which will soon afterwards be the more stable one; a fact which may be perhaps important in the future for the explanation of the analogous phenomena observed in the *separation of two liquid layers* and *the coagulation of a colloidal solution*.

Indeed, the transition at (t_2) presents quite the aspect of a gelatinising colloidal solution. The temperature of this transition point may be determined, but not sharply, at 87°.8. The temperature at which, when the solid substance melts, the liquid may be still kept turbid, owing probably to the presence of the meta-stable plate-like crystals of *S*, was determined at 90°.6; the solidifying temperature (t_1) lies at 82°.2.

That the border liquid, obtained by cooling the isotropous fusion L, differed from L itself, could be demonstrated in more way than one. By heating and cooling we may get so far that, apparently, nothing more of A is visible, but that we have only the border liquid, which on cooling, crystallises immediately to S. Occasionally, the doubly-refracting individuals of A turn up in the mass for a moment to disappear again immediately. However, that isotropous liquid thus obtained is nothing else but A itself, when owing to the temperature variations, all individuals have, like magnets, placed themselves parallel with their (optical) axes and the whole has, consequently, become pseudo-isotropous. This same phenomenon also occurs with the other esters, for instance very beautifully with the nonylate and the myristate. The difference between these pseudo-isotropous phases and the isotropous fused masses L of these substances, is shown by the fact that the pseudo-isomorphous mass of A, and also the doubly-refracting portion of the same has a very thick-fluid consistency; the isotropous fusion L of the laurate has a consistency more like that of glycerol.

As regards the solid phase and its transformation into the liquid condition, it cannot be proved in this case that there exists a continuous transformation between the last solid particlesand the first anisotropous ones. From the velocity, with which the diverse phases usually make room for each other in the microscopic examination, one would feel inclined to believe just the opposite. The thermic observation of the transformation, which generally exhibit only insignificant caloric effects, would, however, make the observer feel more inclined to look upon the matter as an uninterrupted concatenation of more or less stable intermediate conditions, which I have observed previously with *cholesterol-cinnamylate*. A somewhat considerable heat effect occurs in some cases in the crystallisation of the solid phase only; in all other phases the exact transition temperature cannot be determined accurately by the thermic method.

§ 9. *Cholesterol-Nonylate* exhibits microscopically the following phenomena:

Starting from the crystallised substance, this was fused first on an object glass to an isotropous liquid L. On cooling a greyish doubly-refracting liquid phase B appears, which, at a lower temperature, makes room for a very tenaceous, strongly doubly-refracting, mostly yellowish-white phase, A. This phase A is often surrounded by an isotropous border; if pressure is applied to the covering glass or if the mass is stirred with a very thin platinum wire, this isotropous

liquid appears to be identical with *A*, and to be pseudo-isotropous by homoeotropism only. The optical axes of the doubly-refracting modification *A* again place themselves perpendicularly on the surface of the covering glass. On continued cooling *A* becomes increasingly thicker; at last a movement in the mass can be seen only on stirring. After a longer time there are formed from numerous centres in this tenacious mass thin, radiated spherolites, whose velocity of growth is but very small. When a number of these spherolites have formed and the mass is then heated carefully, the spherolites do not melt, but actually *increase* owing to the greater crystallisation-velocity. Soon afterwards — however, they melt, on further heating, to the doubly-refracting phase *A*, *where the circumferences of the spherolites and the black axial crosses are preserved for some time;* so that the whole much resembles a liquid mozaic. Subsequently the phase *B* reappears and afterwards the isotropous fusion *L*. The whole series of phases is traversed in a *reversible* manner; the liquid phase *A*, however may be so much undercooled, that a proper melting or solidifying point of the substance cannot be given. In larger quantities of the substance, the crystallisation does not set in till after some hours, and the substance turns first to a horny mass, which always remains doubly-refracting to finally exhibit local, white spots, from which the spherolite-formation slowly spreads through the entire mass. One would feel inclined to call this transformation of liquid-anisotropous into crystallised substance a *continuous one*, if it were only possible to observe, even for a moment, the intermediate conditions in that transition. As the matter cannot be settled by direct experiment, the transition must be put down, provisionally as a *discontinuous one.*

In this case also, and the same applies to the other cholesterol-esters as well, the *spherolite-structure* of the solid phase is of great importance for this entire transformation of undercooled, anisotropous-liquid condition into the solid one. At the end of this communication I will allude briefly to a few cases from which the particular significance of the spherolite-structure in the transitions between anisotropous-liquid and anisotropous solid phases is shown also plainly in a different manner.

§ 10. *Cholesterol-Palmitate* behaves in quite an analogous manner: I observed one solid phase and three liquid conditions *A*, *B* and *L*; as in the case of the laurate, *B* is generally observed only on warming. The succession of the liquid and solid phases takes place, however comparatively rapidly, so that a real solidifying point may

be observed, which has also been proved by the thermic research. The solid phase crystallises in broad flat needles, when fused and then solidified in conglomerated spherolites. On melting, the thick, doubly-refracting liquid *A* is mostly orientated in regard to the previous solid spherolites.

§ 11. *Cholesterol-Stearate* could not be obtained in a doubly-refracting liquid form: the isotropous fusion always crystallises immediately amid rapid, rotating movements, to small needles, which often consist of a conglomeration of rosettes. It is possible that labile anisotropous phases are formed, owing to strong undercooling or by addition of some admixture [1]).

§ 12. *Cholesterol-Myristiate* lends itself splendidly to the experiment. It behaves mainly in the same manner as the *laurate*; the phase *B* can only be observed on heating, but not on cooling the isotropous fusion *L*. Most brilliant is the formation of large, globular crystal-drops of the modification *A*, also the colour-zone which precedes the formation of *A* from *L*, on cooling. This phase *A* also exhibits the phenomenon of pseudo-isotropism in a particularly distinct form. On the other hand, an important difference between this compound and the laurate is the much smaller velocity with which, on cooling, the spherolites *S* are formed from *A*; in this respect the compound exhibits more similarity with the nonylate. Sometimes it may be observed readily how in the phase *A*, which consists of an enormous number of linked, globular crystal-drops, which all exhibit the black cross of the spherolite crystals, centrifugal current-lines are developed from a number of points in the mass, along which the crystal-drops range themselves. After the lapse of some time those doubly-refracting globules are seen to disappear, while the current-lines have now become rays of the spherolite. Here again, the question arises whether the transformation of the doubly-refracting liquid globules, which are orientated along the current-lines, into the true spherolite form, does not take place continuously, and whether we do not speak of a *sudden* transformation merely because we are not able to observe the stadia traversed in this transformation.

The liquid globules of the phase *A* themselves exhibit much similarity with a kind of liquid spherolites; a few times, I have even been able to observe such "liquid spherolites" of greater dimens-

[1]) Prof. LEHMANN informed me recently that the stearate possesses indeed two labile, anisotropous liquid phases.

ions, which rapidly solidified to solid spherolite crystals. In the case of this compound also, one feels convinced that there must exist a very intimate relation between the spherolite-formation of a substance and its power of forming anisotropous liquid phases; on the nature of this relation, I hope to make a communication later on.

It may, however, be observed, provisionably that in all transformations: liquid $\leftrightarrows$ solid, where serious "phenomena of retardation" may occur, the undercooling, or superfusion, for instance is generally abrogated amid a differentiation of the phase into spherolites. All the cholesterol-derivatives, mentioned in this paper, exhibit this spherolite-formation. In the case of *α-phytosterol-propionate*, I have been able to show, that a complex of a large number of doubly-refracting microscopic spherolites may imitate the optical peculiarities of the liquid phases in process of separation and of the colloidal opalescence. This might lead to the strengthening of the previous conception of the colloidal solidification as a separation-phenomenon of labile liquids.

§ 13. *Cholesterol-Heptylate* contains only *labile* liquid anisotropous phases. It exhibits great similarity with the caprylate described previously: I have only a few times been able to obtain one single thick-fluid phase *A* from the undercooled isotropous fusion *L*. The solid phase crystallises rapidly and in beautiful flat needles, which exhibit high interference colours. On warming, the substance readily migrates towards the colder parts of the object glass.

§ 14. In conclusion, I will communicate a few more points as regards some phenomena, which prove plainly the significance of the spherolite structure for with these questions.

Some time ago, I published a research on the fatty esters from *Phytosterol* from Calabar-fat and stated how they all are wont to crystallise in the spherolite-form from their cooled, isotropous fused mass, while anisotropous liquid phases are *not* observed therein, with the exception of the *normal valerate* which possesses a thick-fluid anisotropous modification, and exhibits the phenomenon of the changeable melting point, which again becomes normal on long keeping; a fact also observed in the case of a few fatty glycerol-esters. Since then, WINDAUS has proved that the phytosterol, extracted from Calabar fat is a mixture of two isomorphous phytosterols, which cannot be separated by crystallisation. Being engaged in preparing the pure fatty esters from the principal of those two phytosterols, namely the *α*-compound (m.p. 136°), I discovered that the fused *propionate* of *α-phytosterol* (m.p. 108°), when cooled rapidly in cold water,

exhibited the most brilliant interference-colours, which is also the case with the cholesterol esters (acetate for instance), which possess *labile* anisotropous liquid phases. The thought naturally at once occurred, to attribute these phenomena to the appearance of liquid crystals in the now *pure* α-phytosterol-ester. A similar behaviour was also shown by perfectly pure *α-phytosterol-acetate*, but with a much less display of colours. It was, however, a remarkable fact, that *α-phytosterol-propionate* even after complete solidification *still retained those colours for an indefinite length of time*, particularly at those sides of the testtube, where the layer of the substance was thinner and had cooled rapidly.

The microscopic investigation now showed that these two substances exhibit extremely rapidly disappearing anisotropous liquid phases or, more probably, *none at all*[1]); but that *the said colour-phenomenon is caused by a very peculiar spherolite-structure.*

In what follows, I have given the description of the solidifying phenomena of the *α-propionate*, and also a figure representing the typical structure of the fused and then cooled compound, such as is present at the coloured sides of the tube.

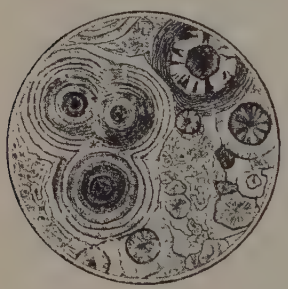


Fig. 2.

If a little of the solid substance is fused on a slide to an isotropous liquid the following will be noticed on cooling. The mass solidifies completely to spherolites, namely to a conglomeration of circular, concentrically grouped figures, which appear connected with a series of girdles. When three spherolites meet, they are joined by means of straight lines which inclose angles of about 120°.

The mass is slightly doubly-refracting and of a greyish colour; the rings and girdles are light greyish on a darker back-ground. Each spherolite exhibits besides a concentric structure, the black cross, but generally very faint. The whole resembles a drawing of polished malachite from the Oeral, or of some polished agates.

[1]) Whereas the *phytosterol*-esters from Calabar fat which, of course, contain a definite amount of the β-homologue, exhibit *no* liquid crystals, the pure α-esters commencing with the butyrate [or perhaps the propionate] did show this phenomenon. This discovery is a powerful argument against the remarks often made in regard to the *cholesterol*-esters, that the remarkable phenomena described are attributable to an admixture of homologous cholesterols. Foreign admixtures prevent as a rule these phenomena altogether: in any case they are rather spoiled than improved.

The walls of the test-tube or the object-glass, which exhibit the said colour-phenomena, have that same structure, but with this difference, that the globular, concentrically deposited spherolites have much smaller dimensions and lie much closer together. Each little spherolite has also a cross; this however, is not dark, but coloured with yellow and violet arms. The spherolite is also coloured in the alternate circle-quadrants.

This ensemble of small, coloured spherolites is the cause of the said brilliant colour-phenomena; they are quite analogous to those which are wont to appear in the case of liquid crystals and remain in existence for an indefinite period. Each of them exhibits one or generally two luminous points in the centre; they exhibit a strong circular polarisation and are left-handed. The whole appears between crossed nicols as a splendid variegated mozaic of coloured cellular parts. The size of each individual is 0.5—1 micron.

The acetate also exhibits something similar, but the spherolites are built more radial and the whole is not at all so distinct.

I hope to contribute more particulars as to these remarkable phytosterol-compounds shortly. I have mentioned them here merely to show the importance of this structure-form for the optical phenomena, observed in the anisotropous phases.

Zaandam, 14 November 1906.

Chemistry. — "*On irreversible phase-transitions in substances which may exhibit more than one liquid condition.*" By Dr. F. M. Jaeger. (Communicated by Prof. Franchimont).

(Communicated in the meeting of November 24, 1906).

§ 1. The fatty esters of *α-Phytosterol* from *Calabar*-fat, which the Phytosterol mostly occurring in the vegetable kingdom, and which has also been isolated from rye and wheat under the name of "sitosterol", exhibit very remarkable properties in more than one respect.

In my previous communication, I alluded briefly to the colour phenomena and the spherolite-structure in the *propionate* and the *acetate*. In the latter I could not observe anisotropous liquid phases; n the former a doubly-refracting phase is discernible just before melting, but it lasts too short a time to allow the accurate measurement of the temperature-traject.

With the following four terms of the series, however, these phenomena are more distinct, and occur under conditions so favourable as

could hardly be realised up to the present in the other known substances. They also exhibit enormous phenomena of retardation in their diverse transitions and often a typical irreversibility thereof, of which I will now communicate some particulars.

§ 2. **Thermometrical behaviour of the fatty α-phytosterol-esters.**

A. α-Phytosterol-n.-Butyrate, on very slowly raising the temperature, melts at 89°.5 to a turbid, doubly-refracting liquid *A*, which at first is very viscous but rapidly becomes thinner and is converted, at 90°.6, into a clear isotropous fusion *L* of the consistency of glycerol.

On cooling the same carefully, the thermometer falls gradually while the isotropous liquid thickens more and more but remains quite clear. At 80° the whole mass crystallises all at once to small crystals *S* with so great a caloric effect that the thermometer goes up to 85°. There is no question now of anisotropous liquid phases at all. These two experiments may be repeated at will but always with the same result. As to the nature of the turbid phase, compare "micro-physical behaviour".

If the isotropous fusion is suddenly cooled in cold water, a bluish-grey coloration appears and a soft, doubly-refracting mass is obtained, which does not become crystalline until after a very long time.

B. α-Phytosterol-Isobutyrate, when treated in the same manner, melts at 101°.4 to a glycerol-like, turbid, doubly-refracting liquid *A*, which gradually assumes the consistency of paraffin-oil and is converted at about 103°.2, apparently continuously, into a clear fusion *L*.

If this is cooled, it certainly becomes gradually thicker but it still remains quite clear and isotropous.

At 80°.4 it becomes turbid and doubly-refracting; this phase is identical with *A*, and it has the consistency of glycerol; at 73° it has become as thick as butter, and at 66° the thermometer can be moved only with difficulty, whilst it may now be drawn into sticky, doubly-refracting threads. At 65° the thermometer suddenly goes up to 68°.8 and the mass crystallises in long, delicate needles *S*.

On rapid cooling of the fused mass, this is converted into a turbid, greasy looking, doubly-refracting mass, which crystallises but very slowly; no colour-phenomena occur.

C. α-Phytosterol-n.-Valerate melts, when in the crystallised condition, at an *uncertain* temperature. At about 48°, the substance commences to soften visibly, at 54° its consistency is that of thick butter, at 80° it is somewhat thinner, at 85° it is actually liquid, but still turbid and doubly-refracting. *All these transformations proceed quite*

continuously. At about 97.°5 the liquid is clear and isotropous; it has then the thickness of paraffin-oil.

If, however, the isotropous fused mass is cooled, the isotropous paraffin-oil-like liquid remains clear to about 87.°3, when a turbid doubly-refracting phase is formed. This, on further cooling, gradually becomes more viscous; at 80° it is as thick as butter, at 66° it can hardly be stirred, and may be drawn into threads. It may be cooled to the temperature of the room without solidifying. It remains in this condition for hours, but after 24 hours it has again become crystalline. The substance, therefore, has no determinable melting or solidifying point.

D. α-Phytosterol-Isovalerate behaves quite analogously to the *n*-valerate. Neither a definite melting point, nor a solidifying point can be observed. The mass softens at about 45°, is anisotropous thick-fluid at 65°, and becomes clear and isotropous at 81°.

On cooling to 78.°1, a beginning of turbidity is noticed, the liquid gradually becomes thicker and is converted at an uncertain temperature into a tenacious sticky, doubly-refracting mass, which after 24 hours has again solidified to a crystalline mass.

§ 3. The thermometrical behaviour of these remarkable substances is represented in the annexed schematic *p-t*-diagram, for the case of the *n-butyrate* and *isobutyrate*. The typical irreversibility of these phenomena is thus seen at once. Moreover in the case of the two valerates, the whole behaviour can be described only as a real, *gradual* transformation, solid $\rightleftarrows$ liquid with an intermediate realisation of an indefinite number of optically-anisotropous liquids.

§ 4. **The micro-physical behaviour of the fatty α-phytosterol esters.** Perhaps, there are no substances known, which exhibit under the microscope the characteristic phenomena of anisotropous liquids in so beautiful and singular a manner as these esters; in this respect the isobutyrate and the valerate excel in particular. In the normal butyrate, the traject, where the liquid crystals are capable of existence is rather too small. For this reason, although the behaviour of the four substances differs in details, I will describe more particularly the behaviour of the *n*-valerate and as to the others, I will state occasionally in what respect they differ from the valerate. In consequence of the totally different circumstances which the microscopic method involves, nothing more is seen of the thermically observed peculiar irreversibility and even progression of the transformations. For the study of the nature of the diverse phase-transformations, the

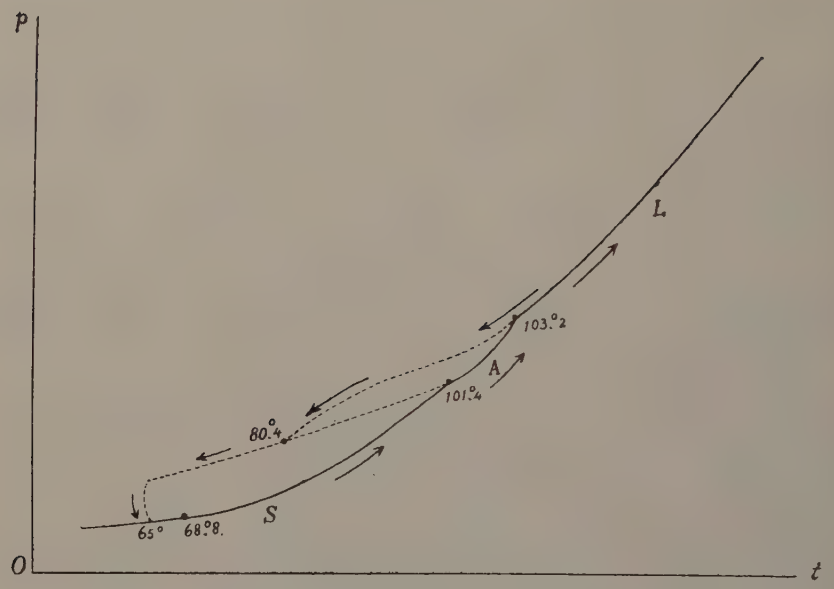


Fig. 1. Schematic p-t-diagram for α-Phytosteryl-Isobutyrate.

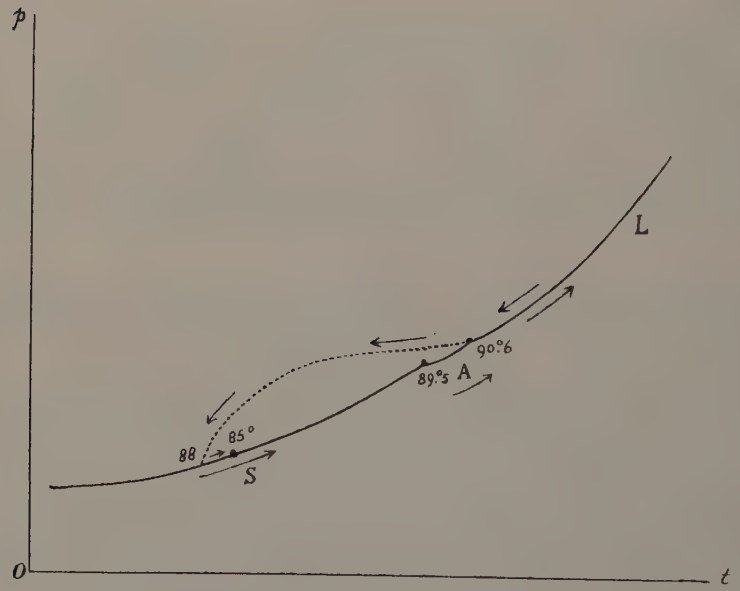


Fig. 2. Schematic p-t-diagram for α-Phytosteryl-n-Butyrate.

thermometric method is certainly preferable to the microscopic one, because in the latter, the delicate changes in temperature cannot be controlled so surely as in the first method. For this reason, the phase-

transformations, when observed microscopically, convey the impression of being more *sudden* than in the thermic observation.

Still, the microscope completes the task of the thermometer in a manner not to be undervalued, at it gives an insight into the structure of the diverse phases and allows one to demonstrate their difference or their identity.

§ 5. If a little of the beautifully crystallised *n-valerate* is carefully melted on an object glass, the substance, at a definite temperature changes, apparently suddenly, into an aggregate of an enormous number of globular, very large and strongly doubly-refracting liquid-drops, which all exhibit the black cross of the spherolites [1]) but can flow really all the same. This condition may be rendered permanent for a long time at will. But they may also amalgamate afterwards to larger, plate-like, highly coloured liquid individuals, somewhat resembling sharply limited crystals. These are frequently multiplets of liquid drops; the demarcations between the separate individuals vary constantly by changes in temperature.

The isotropous border of the mass is very striking. By pressure or by moving the covering glass, also by the sliding currents which we can induce herein by changes in temperature, it may be readily shown that this isotropous border, owing to a parallel orientation of the liquid individuals, is only pseudo-isotropous and really identical with the rest of the phase. Sometimes one may succeed even in communicating this pseudo-isotropous aspect to the entire mass [2]) by

[1]) We can, however, often observe a slanting projection of the optical symmetry axis, which gives the same impression as if we look perpendicularly to one of the optical axes of a biaxial crystal, or on a monoxial crystal cut obliquely to the optical axis. We observe at the same time coloured rings which exhibit an elliptic form. It is very remarkable that, when the phase has become very viscous on cooling, these ellipsoidal drops, provided with rings and slanting but mutually parallel-directed axes may be kept for a long time in an apparently immobile condition in the midst of the pseudo-isotropous or double-refracting liquid. They place themselves mutually like little ellipsoidal magnets.

However, I could observe, that these drops are often not quite ellipsoidal, but that they are sharply broken a little at the one side, just there, where the optical axis is slanting. By turning the object-table, the axial point turns in the same direction as the table, while the black line or cross is preserved. (Added in the English translation Januari 1907).

[2]) The anisotropous-liquid phase has, in the case of the two valerates, an extraordinary tendency to place itself in this pseudo-isotropous condition. We can observe this, because the border of the drop often moves inward with widening of the isotropous-looking line. It is also remarkable to see how the flowing crystals when meeting an air bubble arrange themselves close together, normally on the border thereof.

often repeated warming followed by rapid cooling. This substance is about the best known example of this phenomenon.

§ 6. If now we go on heating very cautiously, the larger flowing crystals and also the smaller drops situated between them are seen to move about rapidly; the larger individuals, which consist mostly of twins or quadruplets, are split up into a multitude of globular drops and these, together with the smaller ones, disappear at a definite temperature entirely in the isotropous liquid, which is now isotropous in *reality*. The globules of the liquid rotate to the right and the left under distortion of the mass, as may be observed from the spiral-shaped transformation of the black cross. Sometimes, before the mass becomes isotropous we may notice a temporary aggrandisement of the plate-like flowing crystals at the expense of the smaller interjacent globules; a result of the momentarily increased crystallisation-velocity due to heating.

§ 7. On cooling the isotropous fusion this is first differentiated into an infinite number of the double-refracting liquid globulus, which here and there amalgamate to the more plate-like flowing crystals. On further cooling, these latter individuals remain in existence notwithstanding the undercooling, while the little globules in the meanwhile unite to the same kind of plate-like individuals. This aggregate, brilliant in higher interference colours becomes in course of time thicker and thicker in consistency while the aggregation, owing to an apparent splitting, becomes more and more finely granulated. But even after the lapse of some hours, the phase remains anisotropous-liquid as may be easily proved by shifting the mass and by the pseudo-isotropous border, which commences to exhibit delicate, double refracting current-lines. In the end when the pseudo-isotropous liquid has passed like the remainder into the same, almost completely immobile aggregation of doubly-refracting individuals, it is, gradually, transformed after a very long time into an aggregate of plates and spherolite-like masses, which possess a strong double refraction.

§ 8. If, after the lapse of some hours, the partially or completely solidified mass is melted cautiously, we sometimes succeed, in the case of the two *valerates*, in keeping the crystals of the phase S (therefore the *solid* crystals) for a few minutes near the isotropous fusion L at a temperature above the highest transition point. This phenomenon is, therefore, again quite homologous to that first observed by me with *cholesterol-laurate* and which might be described as a

heating of a solid substance S above its melting point without fusion taking place. For the present, at least according to existing ideas, this behaviour can only be explained by assuming the presence of a two-component-system with tautomeric transformations subject to a strong retardation.

When the isotropous fusion *L* which has scarcely cooled to a few doubly-refracting drops is melted cautiously, we may observe sometimes that where a moment before the strongly luminous, yellowish-white globules were visible, there are now present greyish globules showing the black cross, which gradually decrease in size and also darken, to disappear finally as (isotropous ?) little globules in the isotropous fusion [1]). This phenomenon, in connection with those of crystallised ferric chloride to be described later, and with similar phenomena observed with the cholesterol esters appears to me to have great significance for the theory of the formation of liquid crystals.

§ 9. Finally, there is something to be observed as to the separation of *α-Phytosterol-valerate* from organic solvents. The substance may be obtained from ethyl acetate + a little alcohol in beautiful, hard, well-formed little crystals. If, however, the saturated *cold* solution in ethyl acetate is mixed with much acetone (in which the substance is but sparingly soluble) the liquid suddenly becomes a milky-white emulsion which deposits the compound *not* as a fine powder, but in the form of a *doubly-refracting, very thick and very sticky liquid.*

I have repeated this precipitation in a hollow object glass under the microscope. The emulsion consists of a very great number of doubly-refracting, globular liquid-globules, which are either moving about rapidly in the liquid, or, when united to larger masses, are quite identical with the ordinary anisotropous phase *A*, when this is cooled to the temperature of the room. These little globules all exhibit the cross of the spherolites, and the doubly-refracting liquids. They soon become solid and then form small needles and spherolitic aggregations. It may be easily proved by stirring that the globules deposited first are liquid; moreover, the doubly-refracting masses often communicate with each other by means of very narrow, doubly-refracting currents, while they often exhibit the phenomena of pseudo-isotropism.

Therefore, we have evidently obtained here the liquid-anisotropous

[1]) Before that happens, we may sometimes see here the globules becoming enlarged to multiplets by amalgamation there larger ones being changed into smaller ones, sometimes here one disappearing in the liquid while very close by new individuals appear.

phase *A* from a solution by rapid precipitation at the temperature of the room, and that in isolated drops! A few other phytosterol esters exhibit analogous phenomena which I will describe later on in a more elaborate communication on these substances.

§ 10. A very remarkable fact in the *n-valerate*, the *iso-valerate* and the *isobutyrate*, is the differentiation of the isotropous fusion into a large number of globular, doubly-refracting liquid drops of considerable dimensions, which like the circles of fat on soup float alongside and over each other and often unite to multiplets, whose separate parts are still recognisable. Wreathed aggregations of the liquid globules are also observed occasionally. In most cases the separate liquid globules exhibit the black cross and the four luminous quadrants grouped centrically. They are, however, also seen to roll about frequently, so that the projection of the optical symmetry axis now takes place excentrically. Owing to the enormous size of the individuals and the low temperature-limits, these esters lend themselves to the study of these phenomena certainly VORLÄNDER's *p*-azoxybenzoic-ethylester.

If the temperature of the mass, when totally differentiated into liquid globules — and the *isobutyrate* is particularly adapted for this differentiation — is slightly raised, the liquid globules are often seen to disappear suddenly just after they have enlarged their limits as it were by an expansion. It is like a soap-bubble bursting by over blowing.

§ 11. Finally, I wish to observe that the thermical transitions just described and particularly those of the two *valerates*, can only be interpreted by assuming a quite continuous progressive change. For all these gradual transformations. either on melting or on solidifying, a measurable time is required and nowhere is to be found any indication of a sudden leap. An exception is, however, afforded by the sudden crystallisation of the two *butyrates*.

§ 12. As regards the differentiation of the fusion *L* into an aggregate of anisotropous liquid globules, I will now make a communication as to an experiment upon the crystallising of *ferric chloride hexahydrate*, which substance exhibits something similar, and which, like most undercooled fusions and like many compounds which exhibit liquid crystals, crystallises in typical spherolites.

If we melt the compound $Fe_2Cl_6 + 12\,H_2O$ cautiously in a little tube, taking care that no water escapes, and a drop of this brownish-

red fusion is put on an object glass, it may be left for hours at the temperature of the room without a trace of crystallisation being noticed. The liquid is now greatly undercooled and exists in a state of metastable equilibrium. For all that, it has the same chemical composition as the solid phase from which it was formed.

On prolonged exposure, *small liquid globules* appear locally in the fairly viscous mass, probably owing to local cooling, or by a spontaneous evaporation of water at those points. These liquid globules are quite isotropous and are surrounded by a delicate aureole having an index of refraction different from that of the rest of the liquid (fig. 3*a*). The observation shows that, optically, they are, practically, no denser than the liquid, and from the fact that they afterwards become, *in their entirety*, a spherolite of the hexahydrate, we must conclude that their chemical composition does not differ from that of the fused mass.

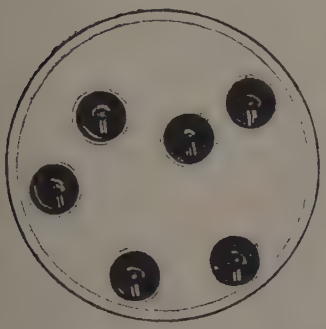


Fig. 3*a*.

These globules of liquid are converted gradually into doubly-refracting masses whose section is that of a regular hexangle with rounded off angles; individual crystals are not yet visible in the doubly-refracting mass and the luminous zone around still appears to exist (fig. 3*b*).

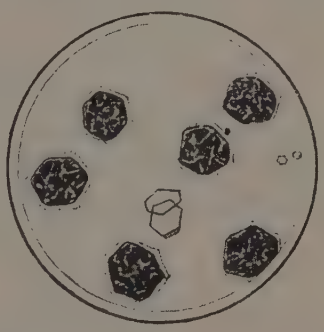


Fig. 3*b*.

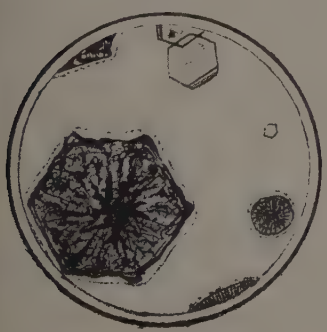


Fig. 3*c*.

Here and there, hexangular, sharply limited, very small plate-shaped crystals are also seen to form in the liquid without previous formation of liquid globules [1]). In the end, the doubly-refracting hexangular mass gets gradually limited by more irregular sides, while a greater differentiation of the mass into light and dark portions points to a crystallisation process commencing and progressing slowly.

[1]) These may, however, be formed perhaps owing to the presence of traces of sal ammoniac.

Finally, we can observe a *spherolite* of the hexahydrate with a radial structure which now grows centrifugally to the large well-known semi-spheroidal spherolites of ferric chloride (fig. 3*c*).

§ 13. This experiment proves that the abrogation of the metastable condition, or at all events of a liquid condition which is possible under the influence of *phenomena* of retardation may happen owing to the formation of *spherolites which are preceded by the differentiation of the fusion into an aggregate of liquid globules.* True, the latter are here isotropous in contrast with the phytosterol esters just described, but the anisotropism of the latter liquids may be caused also by factors which are of secondary importance for the apparently existing connection between: metastability of liquid conditions, their abrogation by spherolite formation and the possible appearance of liquid globules as an intermediate phenomenon. I will just call attention to the fact that if we set aside a solution to crystallise with addition of a substance which retards the crystallisation, this will commence with the separation of originally isotropous liquid globules, so-called globulites, which BEHRENDS and VOGELSANG commenced to study long time ago.

All this leads to the presumption that the formation of the anisotropous liquid phases as aggregates of doubly-refracting liquid globules may have its origin in a kind of *phenomena* of retardation, the nature of which is still unknown to us at the present. Before long, I hope to revert again to this question.

Zaandam, 21 Nov. 1906.

Physics. — "*Some additional remarks on the quantity H and* MAXWELL'S *distribution of velocities.*" By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

§ 1. In these proceedings of Jan. 27th 1906 occur some remarks by me under the title of: "Some remarks on the quantity H in BOLTZMANN'S Vorlesungen über Gastheorie".

My intention is now to add something to these remarks, more particularly in connection with GIBBS' book on Statistical Mechanics [1]), and a paper by Dr. C. H. Wind: "Zur Gastheorie" [2]).

In my above-mentioned paper I specially criticised the proofs given

[1]) J. WILLARD GIBBS "Elementary Principles in Statistical Mechanics", New-York, 1902.

[2]) Wien. Sitzungsber. Bd. 106, p. 21, Jan. 1897.

by BOLTZMANN and JEANS that MAXWELL's distribution of velocities in a gas should give the most probable state, and demonstrated that they wrongly assume an equality of the probabilities a priori that the point of velocity of an arbitrary molecule would fall into an arbitrary element of the space.

The question, however, may be raised whether it would not be possible to interpret the analysis given by BOLTZMANN and JEANS in a somewhat different way, so that avoiding the incorrect fundamental assumption, the result could all the same be retained. And then this proves really to be the case. When the most probable distribution of velocities is sought from the ensemble of equally possible combinations of velocities with equal total energy, we make only use of the fact that the different combinations of velocities *are* equally possible, how they have *got* to be so is after all of no consequence. Or else, it had not been necessary to occupy ourselves with the separate velocities of the molecules and make an assumption as to them.

This way of looking upon the matter is of exactly the same nature as that constantly followed by GIBBS in his above-mentioned work. GIBBS treats in his book all the time instead of a definite system, an ensemble of systems of the same nature and determined mostly by the same number of general coordinates and momenta ($p_1 \ldots p_n$, $q_1 \ldots q_n$), which he follows in their general course. Such an ensemble will best illustrate the behaviour of a system (e.g. a gas-mass), of which only a few data are known and of which the others can assume all kinds of values. He calls such an ensemble *micro-canonical* when all systems, belonging to it, have an energy lying between E and $E + dE$ and for the rest the systems are uniformly distributed over all possibilities of phase or uniformly distributed over the whole *extension-in-phase* the energy of which lies between E and $E + dE$. When the energy of a gas-mass is given (naturally only up to a certain degree of accuracy) we should have reason according to GIBBS to study the microcanonical ensemble determined by this energy, and to consider the gas-mass as taken at random from such an ensemble. The extension-in-phase considered is thought to be determined by $\int dp_1 \ldots dq_n$, but in the case of a gas-mass with simple equal molecules this is proportional to

$$\int dx_1\, dy_1\, dz_1 \ldots dx_n\, dy_n\, dz_n,\, d\dot{x}_1\, d\dot{y}_1\, d\dot{z}_1 \ldots d\dot{x}_n\, d\dot{y}_n\, d\dot{z}_n,$$

so that we may say that every combination of velocities and configuration is of equally frequent occurrence in the ensemble.

It is now easy to see that when the energy is purely kinetic the

same cases occur in such an ensemble, *with regard to the distribution of velocities*, as are considered as equally possible cases by BOLTZMANN and JEANS. The difference in the way of treatment of GIBBS on one side, and that of BOLTZMANN and JEANS on the other consists besides in the fact that the one occupies himself with separate velocities and the other not, in this that GIBBS treats the configuration and the distribution of velocities at the same time (both belong to the idea phase), whereas JEANS treats the latter separately, and BOLTZMANN does not occupy himself with the configuration in this connection.

Every phase of BOLTZMANN (combination of velocities) corresponds with as many phases of GIBBS (combination of velocities and configuration) as the molecules can be placed in different ways with that special combination of velocities. This number being the same for every combination of velocities according to the independence of the distribution of velocities and configuration following from the fundamental assumption, it will be of no consequence, comparing the different combinations of velocities inter se, whether we also take the configuration of the molecules into account or not. So when seeking the most probable distribution of velocities (that, with which the most combinations of velocities coincide), we must arrive at the same result whether we follow GIBBS or BOLTZMANN.

It is obvious that the phases of the microcanonical ensemble meant here are what GIBBS calls the specific phases. GIBBS distinguishes namely between specific and generic phases: in the former we consider as different cases those where we find at the same place and with the same velocity, other, even though quite equal molecules, in the latter we do not. In other words: in the former we consider also the individual molecules, in the second only the number of the molecules. So we may now say that in such a microcanonical ensemble the most probable distribution of velocities and that which will also occur in the great majority of cases (compare JEANS' analysis discussed in the first paper) will be that of MAXWELL. When therefore an arbitrary mass of gas in stationary state may be considered as taken at random out of such a microcanonic ensemble, MAXWELL's distribution of velocities or one closely resembling it will most probably occur in it. In this way a derivation of the law has been obtained to which the original objection no longer applies, though, of course, the assumption of the microcanonical ensemble remains somewhat arbitrary [1]).

[1]) With the more general assumption of a *canonical* ensemble MAXWELL's law is derived by LORENTZ: "Abhandlungen über Theoretische Physik", Lpzg. 1906 I, p. 295.

Finally the question might be raised, when we want to consider the separate velocities, whether it is possible to arrive at the equally possible combinations under discussion on another supposition a priori about the chances of every value for the velocity than the one indicated by BOLTZMANN and JEANS. The supposition must of course be such, that the chance is independent of the direction of the velocity, so that the chance of a velocity c, at which the point of velocity falls into a certain element of volume $d\xi d\eta d\zeta$, may be represented by $f(c)d\xi d\eta d\zeta$. When we moreover assume that the probabilities for the different molecules are independent of each other, the probability of a certain combination of velocities is proportional to $f(c_1)f(c_2)\dots f(c_n)$, and this must remain the same when the kinetic energy L, or because the molecules are assumed to be equal, Σc^2 remains the same. For every change of c_k and c_l into c'_k and c'_l, so that $c^2_k + c^2_l = c'^2_k + c'^2_l$, must $f(c_k).f(c_l) = f(c'_k).f(c'_l)$. This is an equation which frequently occurs in the theory of gases, from which follows $f(c) = ae^{bc^2}$. As a special case follows from this: $f(c) = a$, i. e. the assumption of BOLTZMANN and JEANS, that the probability a priori would be equal for every value of the velocity.

§ 2. In the second place I wish to make some remarks in connection with the proof that BOLTZMANN gives in his "Gastheory", that for an "ungeordnetes" gas with simple suppositions on the nature of the molecules in the stationary state MAXWELL's distribution of velocities is found. Dr. C. H. WIND shows in his above-mentioned paper that in this BOLTZMANN makes a mistake in the calculation of the number of collisions of opposite kind. BOLTZMANN, namely, assumes, that when molecules whose points of velocity lie in an element of volume $d\omega$, collide with others whose points of velocity lie in $d\omega_1$, so that after the collision the former points lie in $d\omega'$ and the latter in $d\omega_1'$, now the elements of volume $d\omega$ and $d\omega'$, $d\omega_1$ and $d\omega_1'$ would be equal, so that now $d\omega'\, d\omega'_1 = d\omega\, d\omega_1$. He further assumes that when molecules collide whose points of velocity lie in $d\omega'$ and $d\omega_1'$, they will be found in $d\omega$ and $d\omega_1$ after the collision. These last collisions he calls collisions of opposite kind. WIND now shows that this assumption is untrue; $d\omega$ is not $= d\omega'$, $d\omega_1$ not $= d\omega'_1$, nor even $d\omega d\omega_1 = d\omega' d\omega_1'$, except when the masses of the two colliding molecules are equal [1]).

Further the points of velocity of colliding molecules which lay in $d\omega'$ and $d\omega_1'$, do not always get to $d\omega$ and $d\omega_1$ after collision,

[1]) I point out here that even then it is not universally true, but only when the elements of volume $d\omega$ and $d\omega_1$ have the shape of rectangular prisms or cylindres whose side or axis has the direction of the normal of collision.

so that another definition is necessary for collisions of opposite kind, viz. such for which the points of velocity get in $d\omega$ and $d\omega_1$ after the collision. WIND proves further that the number of collisions of opposite kind is all the same represented by the expression which BOLTZMANN had found for it.

It is then easy to change (what WIND does not do) the proof given by BOLTZMANN in § 5 of his "Gastheory", that Maxwell's distribution of velocities is the only one possible, in such a way that it is perfectly correct. But the error in question makes itself felt all through BOLTZMANN's book. Already with the proof of the H-theorem given in more analytical form in a footnote to § 5 we have some difficulty in getting rid of this error.

We meet the same thing when the molecules are treated as centres of force, and when they are treated as compound molecules. At the appearance of the second volume of his work, BOLTZMANN had taken notice of WIND's views, but the inaccurate definition for collisions of opposite kind has been retained [1]).

In connection with this error, made by BOLTZMANN in a geometrical treatment of the phenomena of collision, is another error of more analytical nature, so that also JEANS, who treats the matter more analytically, gives a derivation which in my opinion is not altogether correct. Though preferring the geometrical method, BOLTZMANN repeatedly refers to the other [2]). The method would then consist in this, that the components of the velocities after the collision $\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1$ are expressed by $f'(\xi\eta\zeta\xi_1\eta_1\zeta_1)$ and then by means of JACOBI's functional determinant $d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1$ is expressed in $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$. We find then that here this determinant is $= 1$ and so

$$d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1 = d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1 \text{ or } d\omega' d\omega'_1 = d\omega d\omega_1 .$$

The number of collisions of opposite kind $= f'F'_1 d\omega' d\omega'_1 \sigma^2 g \cos\vartheta d\lambda dt$ according to BOLTZMANN, and so also $= f'F'_1 d\omega d\omega_1 \sigma^2 g \cos\vartheta d\lambda dt$. In this the mistake is made, however, that $d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1$ the volume in the space of 6 dimensions that would correspond with the volume $d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$ before the collision, is thought as bounded by planes such as $\xi' = c$, which is not the case. JEANS too equates the products of the differentials, in which according to him, $d\xi' \ldots d\zeta'_1$ being arbitrary, the $d\xi \ldots d\zeta$ must be chosen in such a way, that the values of $\xi' \ldots \zeta'_1$ calculated by the aid of the functions $\xi' = f'(\xi \ldots \zeta_1)$ etc. fall within the limits fixed by $d\xi'$ etc [3]). This, however, is impossible.

1) Cf. § 78, 2nd paragraph.

2) Cf. among others volume I, p. 25 and 27.

3) Cf. "The dynamical Theory of Gases" p. 18.

In my opinion the correct principle that the calculation of the extension occupied by the combinations of the points of velocity after the collision when that before the collision is known and vice versa, would come to the same thing as a transition to other variables in an integration, has not been applied in exactly the correct way. The property in question says that in an integral with transition from the variables $\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1$ to $\xi\eta\zeta\xi_1\eta_1\zeta_1$ the product of the differentials $d\xi' d\eta' d\zeta' d\xi'_1 d\eta'_1 d\zeta'_1$ may be replaced by $\frac{d(\xi'\eta'\zeta'\xi'_1\eta'_1\zeta'_1)}{d(\xi\eta\zeta\xi_1\eta_1\zeta_1)} d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$, if we integrate every time with respect to the corresponding regions, *but these expressions are not equal for all that.* The first expression may be said to represent the elementary volume in the space of 6 dimensions, bounded with regard to $\xi' \ldots \zeta'_1$, the second the elementary volume bounded with regard to $\xi \ldots \zeta_1$ [1]).

We have a simple example when in the space of three dimensions we replace $\int p dx dy dz$, which e.g. represents the weight of a body, by $\int p r^2 \sin\vartheta dr d\vartheta d\varphi$, which represents the same thing, without $dx\,dy\,dz$ having to be equal to $r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi$.

So we have here:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int \left| \frac{d(\xi' - \zeta'_1)}{d(\xi - \zeta_1)} \right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1,$$

which two expresssions represent the "extension" in the space of 6 dimensions after the collision. That before the collision is $\int d\xi d\eta d\zeta d\xi_1 d\eta_1 d\zeta_1$, so that, when the determinant $= 1$, the extension remains unchanged by the collision. This proves really to be the case, as JEANS shows. We may, however also consider this property as a special case of the theorem of LIOUVILLE, and derive it from this [2]). This theorem says, that with an ensemble of identical, mutually independent, mechanic systems, to which HAMILTON's equations of motion apply, $\int dp_1 \ldots dq_n = \int dP_1 \ldots dQ_n$, when $p_1 \ldots q_n$ represent the coordinates and momenta of the systems at an arbitrary point of time, $P_1 \ldots Q_n$ those at the beginning. GIBBS calls this law: the principle of conservation of extension-in-phase, which extension we must now think extended over a space of $2n$ dimensions. When now the two colliding molecules are considered as a system which does not experience any influence of other systems, and it is assumed that during the

[1]) Cf. LORENTZ, l. c. Abhandlung VII.

[2]) As BOLTZMANN cursorily remarks: volume II p. 225.

collisions forces act which only depend on the place of the particles and not on the velocities, we may apply the formula $\int dp'_1 \dots dq'_n = \int dp_1 \dots dq_n$ to an ensemble of such pairs of molecules, the former representing the extension-in-phase after, the latter that before the collision. In the case discussed by BOLTZMANN the masses of these molecules are m and m_1 so that we get:

$$\int dx'\, dy'\, dz'\, m^3\, d\xi'\, d\eta'\, d\zeta'\, dx'_1\, dy'_1\, dz'_1\, m_1^3\, d\xi'_1\, d\eta'_1\, d\zeta'_1 =$$

$$= \int dx\, dy\, dz\, m^3\, d\xi\, d\eta\, d\zeta\, dx'\, dy'\, dz'\, m_1^3\, d\xi'\, d\eta'\, d\zeta'.$$

As we may consider the coordinates during the collision as invariable, it follows from this that:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta.$$

§ 3. However as has been referred to above, we may, without assuming anything about the mechanism of the collision, prove the property by means of the formulae for the final velocities with elastic collision, making use of the functional determinant. Another method is followed by WIND in his above-mentioned paper (the second proof) and by BOLTZMANN (vol. II p. 225 and 226); this method differs in so far from the preceding one, that the changing of the variables takes place by parts (by means of the components of velocity of the centre of gravity), which simplifies the calculation [1]). A third more geometrical method is given by WIND in his first proof. This last method seems best adapted to me to convey an idea of the significance of the principle of conservation of extension-in-phase in this special case. I shall, however, make free to apply a modification which seems an abridgment to me, by also making use of the functional determinant. So it might now also be called a somewhat modified first method.

In the first place I will call attention to the fact that with these phenomena of collision it is necessary to compare infinitely small volumes; if we, therefore, want to use the formula:

$$\int d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1 = \int \left| \frac{d(\xi' \dots \zeta'_1)}{d(\xi \dots \zeta)} \right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$$

[1]) It seems to me that in this proof BOLTZMANN does not abide by what he himself has observed before (§ 27 and § 28, vol. II), viz. that the equality of the differential products means that they may be substituted for each other in integrals. The beginning of § 77 and the assumption of $du\, dv\, dw$, and $dU\, dV\, dW$, as reciprocal elements of volume, is, in my opinion, inconsistent with this

we must take infinitesimals of the 2nd. order. We can, however, also proceed in a somewhat different way. For how is the above formula derived? By making use of the fact, that with a volume $d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$ in the region of the $\xi \ldots \zeta_1$ corresponds a volume

$$\left|\frac{d(\xi' \ldots \zeta'_1)}{d(\xi \ldots \zeta_1)}\right| d\xi\, d\eta\, d\zeta\, d\xi_1\, d\eta_1\, d\zeta_1$$

in the region of the $\xi' \ldots \zeta'_1$, or also that the first mentioned extension, occupied by the representing points in the space of 6 dimensions before the collision, will give rise to the second extension after the collision. We can, therefore very well compare these expressions inter se, without integration, if only the second expression is not interchanged with $d\xi'\, d\eta'\, d\zeta'\, d\xi'_1\, d\eta'_1\, d\zeta'_1$, i. e. the volume element obtained by dividing the extension after the collision in another way.

We now suppose the points of velocity before the collision to be situated in two cylindres, the axes of which are parallel to the normal of collision. The bases of the cylindres are $dOdO_1$ and the heights $d\sigma$ and $d\sigma_1$. The extension occupied by the combinations of the points of velocity is evidently equal to the product of the contents of the cylindres: $dOdO_1\, d\sigma d\sigma_1$. In case of collision the components of the velocities perpendicular to the normal remain unchanged, so the points of velocity are shifted in the cylindres in the direction of the axis, so that σ becomes σ', and σ_1 becomes σ'_1. Between these quantities exist the relations: $\sigma' = \frac{m\sigma + m_1(2\sigma_1 - \sigma)}{m + m_1}$ and $\sigma'_1 = \frac{m_1\sigma_1 + m(2\sigma - \sigma_1)}{m + m_1}$, when m and m_1 denote the masses of the colliding molecules (i.e. the same relations as between the normal initial and final velocities with elastic collision.

If we now wish to calculate the extension after impact we may make use of the fact that dO and dO_1 have not changed, so that we need only examine what happens to $d\sigma d\sigma_1$ or what extension in the region of the $\sigma'\sigma'_1$ corresponds to the extension $d\sigma d\sigma_1$ in the region of the $\sigma\sigma_1$.

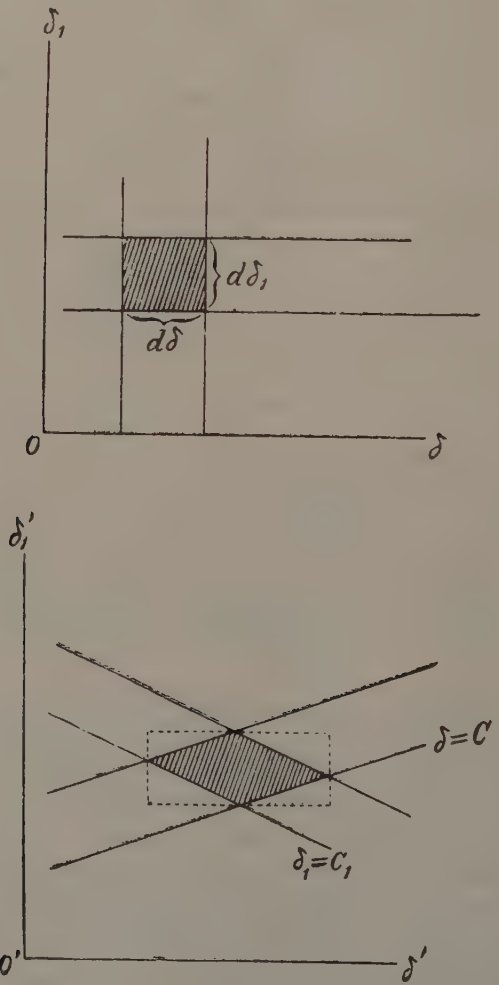
According to the above this is: $\left|\frac{d(\sigma'\sigma'_1)}{d(\sigma\sigma_1)}\right| d\sigma d\sigma_1$, and as it follows from the formulae for σ' and σ'_1 that the absolute value of the determinant $= 1$, the extensions before and after impact are equal.

The extension after the collision is, however, not equal to the product of the cylindres in which the points of velocity will be found after the collision. This will be easily seen with the aid of the geometrical representation given by Wind. The extension before impact may be thought as the product of the extension in the space

of four dimensions $dOdO_1$ and the extension $d\delta d\delta_1$, which we may imagine as a rectangle in the region of the $\delta\delta_1$, when we project them as two mutually normal coordinates in a plane.

Every point in the rectangle represents therefore a number of combinations of velocities with equal δ and δ_1. The sides of the rectangle with equations $\delta = c$ and $\delta_1 = c_1$, correspond in the region of the $\delta'\delta'_1$ with the right lines $m\delta' + m_1(2\delta'_1 - \delta) = (m + m_1)c$ and $m_1\delta'_1 + m(2\delta' - \delta'_1) = (m + m_1)c_1$, so that from the combinations represented by points within the rectangle after the impact others follow represented by points within an oblique parallelogram.

The formula $\left|\frac{d(\delta'\delta'_1)}{d(\delta\delta_1)}\right| = 1$ expresses that the two figures have the same area. Now the extension after impact is equal to this paralel-



logram $\times dOdO_1$ or the product of the two cylindres in which points of velocity were found before impact. The product of the cylindres, in which points of velocity are found after impact is equal to the product of $dOdO_1$ and the area of the rectangle with sides parallel to the axes $O'\sigma'$ and $O'\sigma'_1$ described round the parallellogram under investigation. In this rectangle lie a number of points which have no corresponding points in the first rectangle. Only when $m = m_1$ rectangle and paralellogram coincide.

Collisions of opposite kind, now, are such for which the combinations of velocity before impact are represented by points of the paralellogram in the plane $\sigma' O \sigma'_1$ and after impact by points of the rectangle in the plane $\sigma O \sigma_1$.

Physics. — *"Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XII. *On the gas phase sinking in the liquid phase for binary mixtures."* By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N°. 96*b* from the Physical Laboratory at Leiden.

§ 1. *Introduction.* In what follows we have examined the equilibrium of the gas phase with the liquid phase for binary systems, with which the sinking of the gas phase in the liquid phase may occur.

It lies to hand to treat this problem by the aid of ψ (free energy)-surfaces for the unity of mass of the mixture (VAN DER WAALS, Continuität II p. 27) for different temperatures construed on the coordinates v (volume of the unity of mass of the mixture) and x (quantity of mass of the second component contained in the unity of mass of the mixture).

As VAN DER WAALS (loc. cit.) has already observed, the laws referring to the stability and the coexistence of the phases are the same for these ψ-surfaces as for the more generally used ψ-surfaces for the molecular quantity: in particular also the coexisting phases are indicated by the points of contact of the ψ-surface with a plane which rolls with double contact over the plait in the ψ-surface. In what follows we have chiefly to consider the projections of the connodal curve and of the connodal tangent-chords on the xv-plane.

More particular cases as the occurrence of minimum or maximum critical temperature or minimum or maximum pressure of coexistence we shall leave out of account; we shall further confine ourselves to the case that retrograde condensation of the first kind occurs. Moreover we shall restrict ourselves to temperatures, at which the

appearance of the longitudinal plait does not cause any irregularity [1]). The component with the higher critical temperature (T_k) is chosen as first component; its critical temperature is, accordingly, denoted by T_{k_1}. The special case that $T_{k_2} = 0$, is that of a *gas without cohesion* with molecules having a certain extension. The investigation of the ψ-surfaces becomes simpler for this case. For the present it seems probable to us that helium still possesses some degree of cohesion. We will, however, in a following communication compare the case of a gas without cohesion with what the observations yield concerning mixtures with H_e.

§ 2. *Barotropic pressure and barotropic concentration.* We shall call v and x of the gas phase v_g and x_g, of the liquid phase v_l and x_l. At a temperature T a little below T_{k_1}, we shall always have $v_g > v_l$. For then the plait extends only little on the ψ-surface (see fig. 1), the plaitpoint is near the top of the connodal curve, which is turned to $x = 1$, and all the projections of the connodal tangent-chords deviate little in direction from the v-axis, the angle with the v-axis, $\theta_p = \text{arc tg} \frac{x_g - x_l}{v_g - v_l}$, increases regularly if we go from $x = 0$ along the connodal curve to the plaitpoint, but it has but a small value, when $T_k - T$ is small. Only when we take for T a value a certain amount lower than T_{k1}, the plait extends sufficiently on the ψ-surface to allow that $v_g = v_l$ and $\theta = \frac{\pi}{2}$.

If at a suitable temperature T we have substances as mentioned at the beginning, as e. g. helium and hydrogen at the boiling-point of hydrogen, we shall find the projection of a connodal tangent-chord denoting the equilibrium considered in the xv projection of the gas-liquid-plait on the ψ-surface for T; to reach it we shall have to ascend from $x = 0$ along the connodal curve up to a certain value of the pressure of coexistence p, before θ, which itself is zero for $x = 0$, can become $\frac{\pi}{2}$. A pressure of coexistence $p = p_b$, under which $v_g = v_l$ at the temperature T, we call *a barotropic pressure for that temperature*, the corresponding concentrations of liquid and gas phase *the barotropic concentration of the liquid and of the gas phase at that pressure and that temperature.* For when $v_g - v_l$ with increasing pressure of coexistence p passes through zero at $p = p_b$, we find in equilibria with pressures of coexistence above and below the value p_b the phases to have changed positions under the influence of gravity.

[1]) This will be treated in a following communication.

In order to examine how a barotropic tangent-chord first makes its appearance on the plait on decrease of T, we point out that with extension of the plait from T_{k_1} at first $\frac{d\theta}{dx}$ remains positive all over the liquid branch of the connodal curve, so that at first we have to look for the greatest value of θ at the plaitpoint, where we shall denote its value by θ_{pl}.

When, however, on decrease of T the plait extends over the ψ-surface, this need not continue to be the case, and we may find $\frac{d\theta}{dx}$ alternately positive and negative. This is immediately seen when we notice that this must always be the case when the plait extends all over the ψ-surface.

If with decrease of T the maximum value of θ more and more increases, and T has fallen so low, that the maximum of θ somewhere in the plait has just ascended to $\frac{\pi}{2}$, then at this T the condition for the barotropic equilibrium $v_g = v_e$ will be satisfied just for the corresponding tangent-chord, and only for this tangent-chord. The *higher barotropic limiting temperature* is then reached. On further decrease of temperature the barotropic tangent-chord will then split into two parallel barotropic tangent-chords, the *higher* and the *lower* tangent-chord, which at first continue to diverge with further falling temperature, so that the higher barotropic tangent-chord may even vanish from the plait through a *barotropic plaitpoint*, and then, at a lower temperature, make its appearance again through a barotropic plaitpoint[1]).

At still lower temperature it follows from the broadening of the plait in the direction of the v-axis, which at sufficiently low temperature renders the occurrence of a barotropic tangent-chord impossible, that the maximum of θ falls again, and the barotropic tangent-chords draw again nearer to each other. At $\theta_{max} = \frac{\pi}{2}$ the tangent-chords coincide again, and the *lower barotropic limiting temperature* is reached. At lower temperatures $v_g = v_l$ is no longer to be realized, and v_g is always $> v_l$.

Figs. 2, 3 and 4 represent different cases schematically. In the spacial diagram of the ψ-surfaces for different temperatures the barotropic tangent-chords supplemented with the portions of the con-

[1]) The latter supposes that T_{k_1}/T_{k_2} is not very great; in accepting the contrary we would come in conflict with the supposition that the longitudinal plait does not become of influence. Moreover we preliminarily leave out of account the case that both barotropic tangent-chords follow one another in disappearing or appearing through a barotropic plaitpoint. [Added in the translation].

nodal curves between the lower and the higher tangent-chords form together a closed surface, which bounds the *barotropic region.*

If on the other hand $\theta_{max} = \theta_{pl}$ remains, till it has reached or exceeded the value $\frac{\pi}{2}$, and if not a second maximum value for $\theta > \frac{\pi}{2}$ occurs on the plait, a barotropic plaitpoint will occur at the higher barotropic limiting temperature, whereas at lower temperature a *single* barotropic tangent-chord on the plait indicates the equilibrium with $v_g = v_l$. With decreasing temperature this barotropic tangent-chord will at first move along the plait starting from the plaitpoint, but at lower temperatures it will return, and finally (the occurrence of a longitudinal plait being left out of consideration) it will disappear from the plait through a barotropic plaitpoint at the lower barotropic limiting temperature. In this case the barotropic region is bounded on the side towards which the plait extends by barotropic tangent-chords, on the other side by the portions of the connodal curve which are cut off.

It follows from the above that — when the occurrence of barotropic tangent-chords on the ψ-surfaces for a definite pair of substances is attended by the occurrence of barotropic plaitpoints — if $T_b > T_{bpls}$ (*higher baratropic plaitpoint temperature*) or $T_b < T_{bpli}$ *lower barotropic plaitpoint temperature* there always exists at the same time a higher and a lower barotropic tangent-chord; if $T_{bpls} > T_b > T_{bpli}$ there exists only one barotropic tangent-chord.

The nature of the barotropic phenomenon for He and H_2 may serve for arriving at an estimation of the critical temperature of He. According to the investigation of one of us (K. See Comm. N°. 96 c.) it is probable that the appearance of *a single* barotropic tangent-chord for He—H_2 at the temperature of boiling hydrogen would point to $T_{kHe} <$ about 2°, whereas on the other hand when T_{kHe} is higher, a higher and a lower barotropic tangent-chord is to be expected. Further that, as was already observed in Comm. No. 96 a. (Nov. '06) a barotropic tangent-chord can only appear in the gas-liquid-plait when very unusual relations are satisfied between the properties of the mixed substances, which for the present will most likely only be observed for He and H_2.

Whether it is possible that more than one barotropic region occurs, and whether one or more barotropic tangent-chords can move from the plaitpoint past the critical point of contact, is still to be examined. Also whether it is possible that the lower barotropic limiting temperature descends lower than T_{k_2}, so that fig. 5 might be realised. With regard to these questions too it is only of practical importance to

know in how far the properties of He and H_2 create that possibility.

§ 3. *Barotropic phenomena at the compression of a mixture of definite concentration.* What will take place in this case is easy to be derived from the foregoing survey of the different equilibria which are possible at a same temperature. For the further discussion we have to trace the *isomignic* line, the line of equal concentration ($x =$ const.) for this mixture, and to examine the section with the connodal curve, the successive chords, and finally again with the connodal curve.

In the description of the barotropic phenomena we shall confine ourselves to the more complicated case, that at the T considered both a higher and a lower barotropic tangent-chord occur, after which it will be easy to survey the phenomena when only one barotropic tangent-chord appears.

To distinguish the different cases we must divide the liquid branch of the connodal curve at T into an *infra-* ($x = 0$ to $x = x_{lbiT}$, *lower barotropic concentration of the liquid phase at* T), *inter-* (x_{lbiT} to x_{lbsT}) and *supra-* ($x = x_{lbsT}$ to $x = x_{pl}$)*-barotropic* part, and the gasbranch into the three corresponding pieces falling within and on either side of the region between the two barotropic tangent-chords (the lower b_{iT} and the higher b_{sT}) at that temperature.

Whether the phenomena of retrograde condensation attend those of the barotropic change of phase or not depends on this: whether both barotropic concentrations of the gas phases fall below the plait-point concentration or not.

Let us restrict ourselves in this description to the case that this complication does not present itself or let us only consider mixtures for which $x < x_{pl}$. On compression the first liquid accumulates in the lower part of the tube for $x < x_{gbiT}$ and for $x_R > x > x_{gbsT}$, and in the higher part for $x_{gbsT} > x > x_{gbiT}$. On further compression, when $x_{gbiT} > x_{lbsT}$, change of phase will take place *once* for mixtures of the concentration x, so that $x_{gbsT} > x > x_{gbiT}$ or $x_{lbsT} > x > x_{lbiT}$; it will take place *twice* for mixtures of the concentration x, so that $x_{gbiT} > x > x_{lbsT}$. So the last remains of the gasphase will vanish above for $x < x_{lbiT}$ and for $x_{pl} > x > x_{lbsT}$, and below for $x_{lbsT} > x > x_{lbiT}$. If it is possible that over a certain range of temperature the barotropic tangent-chords get so far apart that $x_{lbsT} > x_{gbiT}$, change of phase will again take place *once* for these temperatures for mixtures of the concentration x, so that $x_{gbsT} > x > x_{lbsT}$ or $x_{gbiT} > x > x_{lbiT}$.

This description will, of course, only be applicable to He and H_2 when the suppositions mentioned prove to be satisfied.

§ 4. *Disturbances by capillary action.* As is always tacitly assumed in the application of the ψ-surface when the reverse is not expressly stated, the curvature of the surfaces of separation of the phases is put zero in the foregoing discussion. If the curvature may not be neglected, e. g. at the compression of a mixture in a narrow tube, then, when the barotropic pressure is exceeded, the phase which has thus become heavier, will only sink through the lighter phase under it, when the equilibrium has become labile taking the capillary energy of the surface of separation into account. For this it is required that θ_p has become larger than $\frac{\pi}{2}$ to an amount of $\Delta\theta_{cap}$, which will depend on the capillary energy of the surface of separation and the diameter of the tube in which the experiment is made. Thus capillarity causes a retardation of the appearance of the barotropic phenomenon: both with increase and with decrease of pressure the barotropic tangent-chord must be exceeded by increase or decrease of pressure to a certain amount, before the two phases interchange positions. In this way the difference of pressure mentioned in Comm. N°. 96^{7}, (Nov. 1906, p. 460) between the sinking of the gas phase chiefly consisting of helium and its rising again at expansion (49 and 32 atms.) is e. g. to be explained by the aid of the following suppositions which are admissible for a first estimation.

1. that at $-253°$ and 32, resp. 49 atms. He is in corresponding state with H_2 at 150° and 160, resp. 245 atm., in agreement with the assumptions $M_{He}v_{kHe} = \frac{1}{4}M_{H}v_{kH}$ according to the ratio of the molecular refractive powers, $T_{kHe} = 1°.5$ (according to Olszewski $< 1°.7$); if the gas phase consisted only of He (molec. weight 4), the density at the temperature and pressures mentioned would be 0.062, resp. 0.081, and if moreover the liquid phase had the same density with the two pressures, $\Delta\theta_{cap}$ would have to correspond to a difference of density of $\pm$ 0.01; owing to the fact that the two last mentioned suppositions are not satisfied, the difference of density will be smaller;

2. that the capillary energy of the surface of separation between the phases coexisting at the above temperature and pressures is not many times smaller (or greater) than that of liquid hydrogen at that temperature in equilibrium with its saturated vapour, and that the latter may be derived from that of nitrogen [1]) by the aid of the principle of corresponding states. The gas bubble will then in a tube like that in which the experiment described in Comm. N°. 96*a* was made (int. diam. 8 mm.) only sink through the liquid or rise again, when

[1]) Baly and Donnan, Trans. Chem. Soc. 81 (1902) p. 907.

Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "Contribution to the knowledge of the ψ-surface of van der Waals. XII. On the gasphase sinking in the liquid phase for binary mixtures."

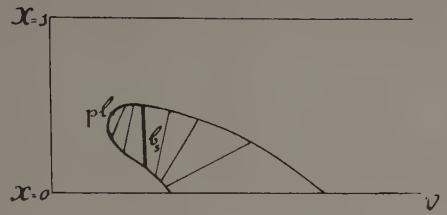


Fig. 2.

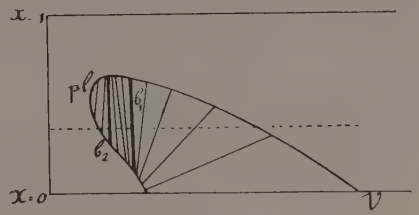


Fig. 3.

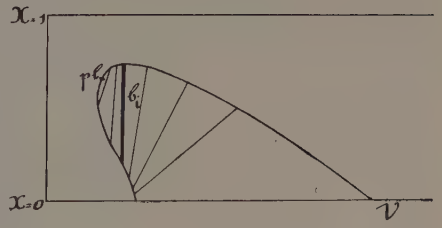


Fig. 4.

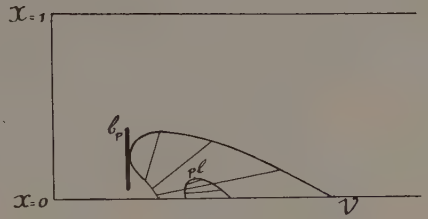


Fig. 1.

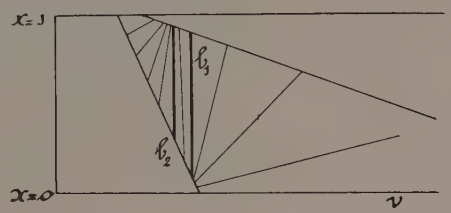


Fig. 5.

the difference of the radii of curvature of the tops of the bounding menisci exceeds that between 3 and 5 mm.

At those temperatures for which $\theta_{max} < \frac{\pi}{2} + \Delta\theta_{cap}$, the phenomenon of the phase which is uppermost at low pressure, sinking and rising again does not make its appearance in consequence of gravity alone. If this condition is satisfied for mixtures of a definite pair of substances for every temperature between the lower and the higher barotropic limiting temperature, the phenomenon could only be realised for these mixtures by the aid of a suitable stirrer.

§ 5. *Remarks on further experiments with helium and hydrogen.*

a. In the experiments mentioned in Comm. N°. 96^a the gas phase proved to remain below on compression to the highest pressure which the apparatus will allow. When we repeat these experiments at a higher temperature (which may e. g. be obtained by boiling the hydrogen of the bath under higher pressure[1])) it is to be expected that the barotropic pressure will first rise, as in the beginning starting from -253° the gas phase will continue to expand more strongly than the liquid phase. At higher temperature the liquid phase begins to expand more strongly than the gas phase, but the mutual solubility plays already such an important rôle then that a definite expectation cannot be expressed, unless this, that on account of the retreating of the plait and the impossibility of the barotropic tangent-chord to reach the side of the hydrogen, the higher barotropic limiting temperature may be pretty soon reached. Also in connection with the estimation, which may be made from this concerning T_{kHe}, it will be of importance to investigate whether with a suitable concentration and at a suitable higher temperature we may observe *the liquid phase sinking after it had first risen.* That the phenomena at higher temperature, if the glass tube used should prove strong enough to bear the pressure, should be prevented by capillary action, is not probable, as capillarity together with the differences of density decreases at higher temperature; moreover in spite of capillarity the phenomena might be realised by the aid of a suitable stirrer.

b. With decrease of temperature the limit is soon reached at which we meet with the solid phase. The question rises whether then the phenomenon: the *solid phase, (the solid hydrogen) floating on the gas phase (chiefly the as yet still gaslike helium)*, might not be realised.

[1]) Or by using the vapour from boiling hydrogen in a separate vessel [added in the translation].

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIII. *On the conditions for the sinking and again rising of the gas phase in the liquid phase for binary mixtures,*" by Dr. W. H. KEESOM. Communication N°. 96*c* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

§ 1. *Introduction.* As has been observed in Communication N°. 96*b* (See the preceding paper) (cf. Comm. N°. 96*a*, Nov. '06, p. 459, note 1) it lies to hand, to take as point of issue the ψ-surface for the unity of mass of the mixture considered, in the investigation according to VAN DER WAALS' theory of binary mixtures, of the sinking and subsequent rising of the gas phase in the liquid phase, i.e. the barotropic phenomenon. Two coexisting phases of equal density are joined on this ψ-surface by a tangent-chord whose projection on the x, v-plane [1]) is parallel to the x-axis. It has already been observed in Comm. N°. 96*b*, that with decrease of temperature starting from the critical temperature of the first (least volatile) component such a barotropic tangent-chord may make its appearance in two ways:

a. by the angle of inclination of the tangent to the plait in the plaitpoint, θ_{pl}, reaching the value of $\frac{\pi}{2}$ at a certain temperature T_{bpl} and by its exceeding this value at lower temperature.

b. by θ showing a maximum and a minimum on the plait at a certain temperature, and by this maximum reaching or exceeding the value of $\frac{\pi}{2}$. Also in this latter case one of the two barotropic tangents-chords which then appear, might reach the plaitpoint at lower temperature, and thus become $\theta_{pl} = \frac{\pi}{2}$.

In both cases in which $\theta_{pl} = \frac{\pi}{2}$ at a certain temperature it should be expected apart from complications as e. g. a longitudinal plait etc. (cf. Comm. N°. 96*b*, p. 502), the description of which will be given later on, that θ_{pl} becomes again $= \frac{\pi}{2}$ for mixtures of the same substances at a lower temperature.

In the first part of this paper the conditions are discussed on which a plaitpoint with $\theta_{pl} = \frac{\pi}{2}$, barotropic plaitpoint, occurs on the ψ-sur-

[1]) Cf. for the meaning of x and v Comm. N°. 96*b*.

face, whereas in the second part the conditions are treated for the appearance of a barotropic tangent-chord on the plait.

A. On the conditions for the occurrence of a barotropic-plaitpoint.

§ 2. In a barotropic plaitpoint the isobar, which in a plaitpoint always touches the plait, must run parallel to the x-axis. This gives the condition:

$$\left(\frac{\partial^2\psi}{\partial x \partial v}\right) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

Moreover a section $v = v_{pl}$ of the ψ-surface with the limiting position of the tangent-chord must then have a contact of the 3rd order. This furnishes:

$$\left(\frac{\partial^2\psi}{\partial x^2}\right) = 0 \quad , \quad \left(\frac{\partial^3\psi}{\partial x^3}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1\,b \text{ and } c)$$

The two conditions (1 b) and (1 c) follow also by applying (1 a) to the general relations for the plaitpoint of Comm. N°. 75 (Dec. 1901) p. 294.

The same may be obtained from the property of the barotropic points on the connodal curve that there $\left(\frac{\partial\psi}{\partial x}\right)$ along the connodal shows a maximum or minimum [1]), so that the substitution-curve $\left(\frac{\partial\psi}{\partial c}\right) = \text{const.}$ (see for the substitution curves on the ψ-surface for the molecular quantity Comm. N°. 59[7]), touches the connodal line in these points.

§ 3. For a first investigation we shall use VAN DER WAALS' equation of state:

$$p = \frac{R_x T}{v - b_x} - \frac{a_x}{v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

with an a_x and b_x not depending on v and T for a definite x. In this:

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[1]) This property for coexistence with $v_2 = v_1$ is analogous to the property that $\left(\frac{\partial\psi}{\partial v}\right) = -p$ along the connodal line is a minimum or a maximum for coexisting phases with $x_2 = x_1$. In the same way the mean value of $\left(\frac{\partial\psi}{\partial x}\right)$ along an isometric line $v = v_b$, which joins two barotropic phases on the ψ-surface, is equal to the value of $\left(\frac{\partial\psi}{\partial x}\right)$ for these phases.

$$R_x = R_1(1-x) + R_2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

if $R_1 = R/M_1$, $R_2 = R/M_2$, R representing the molecular gas-constant, M_1 and M_2 representing the molecular weights; we put for this first investigation $a_{12} = \sqrt{a_{11}\, a_{22}}$, so that

$$a_x = \{\sqrt{a_{11}} \cdot (1-x) + \sqrt{a_{22}} \cdot x\}^2 \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

and when we put for the molecular volumes $2b_{12M} = b_{11M} + b_{22M}$, the relation for b_x given by VAN DER WAALS Contin. II p. 27, reduces to:

$$b_x = b_{11}(1-x) + b_{22}\, x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3c)$$

We get then (VAN DER WAALS Contin. II p. 28):

$$\psi = -R_x T \ln(v-b_x) - \frac{a_x}{v} + T\{R_1(1-x)\ln(1-x) + R_2\, x \ln x\} \quad . \quad (4)$$

§ 4. Taking equations (3) into consideration, and putting

$$\frac{b_{22}-b_{11}}{v-b} = u, \quad x = \frac{1+z}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

we get by the conditions (1):

$$R_2 \cdot \frac{1+z}{2}\left\{u + \frac{2}{1+z}\right\} + R_1 \frac{1-z}{2}\left\{u - \frac{2}{1-z}\right\} = \frac{v-b}{Tv^2}\frac{da}{dx} \quad . \quad . \quad . \quad . \quad (6a)$$

$$R_2 \cdot \frac{1+z}{2}\left\{u + \frac{2}{1+z}\right\}^2 + R_1 \frac{1-z}{2}\left\{u - \frac{2}{1-z}\right\}^2 = \frac{1}{Tv}\frac{d^2a}{dx^2} \quad . \quad . \quad . \quad . \quad (6b)$$

$$R_2 \cdot \frac{1+z}{2}\left\{u + \frac{2}{1+z}\right\}^2\left\{u - \frac{1}{1+z}\right\} + R_1 \frac{1-z}{2}\left\{u - \frac{2}{1-z}\right\}^2\left\{u + \frac{1}{1-z}\right\} = 0 \quad (6c)$$

These equations are sufficient to calculate the data for a barotropic plaitpoint x_{bpl}, v_{bpl}, T_{bpl} for a definite pair of substances. Eliminating T from (6a) and (6b), we get, taking (6c) into consideration and putting:

$$(\sqrt{a_{22}} + \sqrt{a_{11}}) / (\sqrt{a_{22}} - \sqrt{a_{11}}) = \mu \quad . \quad . \quad . \quad . \quad (7a)$$

$$\tfrac{1}{2}(v-b)\left\{u + \frac{2}{1+z}\right\}\left\{u - \frac{2}{1-z}\right\}(\mu+z) + v\left\{u + \frac{4z}{1-z^2}\right\} = 0, \quad (8)$$

while elimination of v from this equation and (5), putting:

$$(b_{22}+b_{11}) / (b_{22}-b_{11}) = \nu \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

yields:

$$\tfrac{1}{2}\left\{u + \frac{2}{1+z}\right\}\left\{u - \frac{2}{1-z}\right\}(\mu+z) + \left\{u + \frac{4z}{1-z^2}\right\}\{\tfrac{1}{2}(\nu+z)\,u + 1\} = 0 \quad . \quad (9)$$

From this equation with (6c): z_{bpl} may be found for given R_2/R_1, μ and ν, after which x_{bpl}, v_{bpl} and T_{bpl}, as well as p_{bpl} follow easily.

§ 5. That a barotropic plaitpoint exists on the liquid-gas-plait with the assumed suppositions (2), (3b), (3c) and with suitable

values of the constants, appears as follows: for $z = 0.5$, $R_2/R_1 = {}^1/_2$, $b_{22}/b_{11} = {}^1/_8$, (6c) yields: $u = -1.957$, after which (9) yields: $\mu = -1.176$, so that $a_{22}/a_{11} = 0.00653$. Thus we find for a mixture of two substances with $M_2 = 2\,M_1$, $v_{k_2} = {}^1/_8\,v_{k_1}$ (so that the ratio of the molecular critical volumes is ${}^1/_4$), $T_{k_2} = 0.052\,T_{k_1}$, a barotropic plaitpoint for $v_{bpl} = 0.26\,v_{k_1}$, $T_{bpl} = 0.80\,T_{k_1}$, $p_{bpl} = 4.8\,p_{k_1}$.

(To be continued).

ERRATUM.

In the Proceedings of the meeting of September 29, 1906.

p. 209, line 15 from the bottom: for § 10 read § 9.

p. 210, Table I, line 5 and 4 from the bottom, for: 5 July read 6 July.

„ 3 from the bottom, for 3 March '05 read 3 March '06.

(January 24, 1907).